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PB80-157217

# Effects of Sulfuric Acid Rain on Two Model Hardwood Forests: Throughfall, Litter Leachate, and Soil Solution

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Jan 80

United States
Environmental Protection
Agency

Environmental Research
Laboratory
Corvallis OR 97330

EPA-600/3-80-014
January 1980

Research and Development

PB80-157217

EPA

# Effects of Sulfuric Acid Rain on Two Model Hardwood Forests

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**TECHNICAL REPORT DATA**
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| 1. REPORT NO. | 2. | 3. RECIPIENT'S ACCESSION NO. |
|---|---|---|
| EPA-600/3-80-014 | | PB 80 157217 |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| Effects of Sulfuric Acid Rain on Two Model Hardwood Forests: Throughfall, Litter Leachate, and Soil Solution | January 1980 issuing date |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| Jeffrey J. Lee and David E. Weber | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT NO. |
| Environmental Research Laboratory<br>U.S. Environmental Protection Agency<br>200 S.W. 35th Street<br>Corvallis, OR 97330 | 11. CONTRACT/GRANT NO. |
| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPORT AND PERIOD COVERED |
| Environmental Research Laboratory<br>U.S. Environmental Protection Agency<br>200 S.W. 35th Street<br>Corvallis, OR 97330 | Final, 1975-1979 |
| | 14. SPONSORING AGENCY CODE<br>EPA/600/02 |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Simulated sulfuric acid rain (pH 3.0, 3.5, 4.5, and 5.6) was applied to model forests containing either sugar maple (Acer saccharum) or red alder (Alnus rubra). Water samples were collected above and below the canopy, below the litter, and from 20 cm and 1 m below the surface of the soil. While throughfall chemistry was not very different from rain chemistry, the litter leachate (the actual input to the soil) had consistently higher concentrations of calcium and magnesium, and higher pH than the acid rain. For the first 6 months, sulfate absorbtion by the soil prevented any apparent differences in sulfate, calcium, or magnesium concentrations in the 20-cm soil solution among plots receiving acid or control rain treatments. Sulfate concentrations on plots receiving the most acid rain (pH 3.0) then became increasingly higher than on the other plots until after 3 years, they were approximately equal to sulfate concentrations in the rain. Twenty-cm soil solutions corresponding to the pH 3.5 and 4.0 treatments responded similarly starting respectively 1 year and 2 years after initiation of exposure to acid rain. Increased calcium and magnesium concentrations and lowered pH in 20-cm soil solution occurred simultaneously with increased sulfate concentrations. No acid rain related effects were evident in the 1-m soil solution even after 3.5 years exposure to pH 3.0 sulfuric acid rain. Cation responses to increased anion concentrations followed those predicted by a computer simulation model. However, sulfate concentrations in 20-cm soil solutions increased considerably faster than predicted by a Langmuir formulation of sulfate absorbtion.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Rainfall, pollution, sulfuric acid, sulfates, ecology, forest trees, soil chemistry, and computerized simulation | Acid rain, bioyeochemical cycles, sugar maple, red alder, and sulfate absorbtion | 06/F<br>07/B |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| Release to public | Unclassified | |
| | 20. SECURITY CLASS *(This page)* Unclassified | 22. PRICE |

EPA Form 2220-1 (Rev. 4-77)

EPA-600/3-80-014
January 1980

# EFFECTS OF SULFURIC ACID RAIN ON TWO MODEL HARDWOOD FORESTS: THROUGHFALL, LITTER LEACHATE, AND SOIL SOLUTION

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## FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its 15 major field installations, one of which is the Corvallis Environmental Research Laboratory.

The primary mission of the Corvallis Laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects and control of pollutants in lakes and streams; and the development of predictive models on the movement of pollutants in the biosphere.

This report describes the effects of simulated sulfuric acid rain on experimental model hardwood forests, and compares the results to the predictions of a computer simulation model. This work was undertaken as part of a research program at CERL to determine the effects of acid rain on forest ecosystems.

Thomas A. Murphy, Director
Corvallis Environmental Research Laboratory

## ABSTRACT

Simulated sulfuric acid rain was applied to model forests containing either sugar maple (Acer saccharum) or red alder (Alnus rubra). One set of four plots (two alder and two maple) received a control rain consisting of a stock solution equilibrated with atmospheric $CO_2$ to approximately pH 5.6. For three sets of four plots, sufficient $H_2SO_4$ was added to the stock solution to lower the pH to 3.0, 3.5, or 4.0. Nozzles were used to apply simulated acid rain at the rate of 2.8 mm/hr (maple) or 3.7 mm/hr (alder) for three hours per day, three days per week, throughout the year. Water samples were collected above and below the canopy, below the litter layer, and from 20-cm and 1-m depths below the surface of the soil.

While throughfall chemistry was not very different from rain chemistry, the litter leachate (the actual input to the soil) had consistently higher concentrations of calcium and magnesium, and higher pH, than the acid rain.

For the first six months, sulfate absorption by the soil prevented any apparent differences in sulfate, calcium, or magnesium concentrations among plots receiving either acid or control treatments. Sulfate concentrations on plots receiving the most acid rain (pH 3.0) then became increasingly higher than on the other plots until, after three years, they were approximately equal to sulfate concentrations in the rain. Soil solutions corresponding to the pH 3.5 and pH 4.0 treatments responded similarly starting one year and two years, respectively, after initiation of exposure to acid rain. Increased calcium and magnesium concentrations and lowered pH in 20-cm soil solution occurred simultaneously with increased sulfate concentrations. At a depth of one meter, no acid rain related effects were evident even after 3.5 years exposure to pH 3.0 sulfuric acid rain.

Comparisons of the data with the predictions of a computer simulation model indicated that soil properties obtained under laboratory conditions can be used with established relationships to predict cation concentrations in soil solutions associated with increased anion concentrations from acid rain. However, sulfate concentrations in the 20-cm soil solution increased considerably faster than predicted by using laboratory values in a Langmuir representation of sulfate absorption.

This report covers a period from June, 1976 through August, 1979.

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# SECTION 1

# INTRODUCTION

Rainfall over large portions of Europe and North America has become increasingly acidic during the past thirty years.[1-7] The increased acidity of precipitation is primarily due to higher concentrations of sulfuric and nitric acids derived from the air pollutants sulfur dioxide ($SO_2$) and oxides of nitrogen ($NO_x$). Although precipitation may be acidified by a local emission source, transport over hundreds and even thousands of kilometers is common. Acid precipitation thus tends to be regional and chronic.[1,5,6,7] With the increased use of fossil fuels, precipitation will probably continue to become more acidic. Currently, all states east of the Mississippi River regularly receive precipitation which is more acidic than the expected value of pH 5.6 for carbonic acid rain.[3,5,6] In the northeastern United States, pH 4.2 is typical of winter precipitation; for summer rains, pH 3.5 is typical.[6] Acid precipitation is not limited to the east, but also occurs in the western U.S.[8,9,10]

The impact of acid precipitation on agricultural and forest ecosystems is not understood. The potential effects of chronic, long term, exposure of forest soils to acid precipitation have been identified as a major concern since, compared to agricultural soils, forest soils are relatively unmanaged.[11,12,13] Increased anion loading of forest soils can, theoretically, cause increased concentrations of cations, both bases and $H^+$, in soil solutions, and, eventually, lead to acidification of soils.[7,14-17] Leaching of bases and acidification of soils by acid rain have been observed,[2,18-21] as has increased mineral weathering.[22-25] Increased soil acidity was thought to be a possible cause of decreased forest productivity in Sweden.[26,27]

Before reaching the forest soil, precipitation percolates through the forest canopy and litter layer. Throughfall from canopies of deciduous trees[2,28-38] and leachates from hardwood litter layers[39] tend to have higher pH values, higher Ca and Mg concentrations, and lower volumes than incident acid precipitation. Any study of the effects of acid precipitation on forest soils must consider the differences in quality and quantity between precipitation and the actual input to the soil, the litter leachate. Similarly, any study of biological processes in forest litter or soil must consider the chemical environment as determined by the litter leachate or soil solution.

At EPA's Corvallis Environmental Research Laboratory in Oregon, we have studied the effects of simulated sulfuric acid rain on nutrient cycling in two types of model hardwood forest ecosystems.[40] As part of this study, rainwater has been regularly collected above and below the canopy, below the litter layer, and at two depths in the soil during a period of more than three years. In this paper, we report on the chemical changes in acid rain as it percolates

through the ecosystem. The concentrations of divalent cations ($Ca^{++}$ plus $Mg^{++}$, equivalent basis) and $SO_4^{--}$ in the soil solution 20 cm below the surface are compared with the predictions of a computer simulation model, LEACH.[17,41]

## SECTION 2

## CONCLUSIONS

A well developed hardwood canopy and litter layer can significantly raise the pH and increase concentrations of bases in rainwater. This will result in a decreased tendency for acid rain to acidify forest soils.

Increased anion concentrations in soil solutions will cause increased concentrations of cations, generally including both bases and hydrogen ions. However, sulfuric acid rain might not cause significantly higher sulfate concentrations in soil solutions until the ability of the soil to absorb sulfate is exhausted. The response of soil solutions to nitric acid rain would be more rapid.

Soil properties identified under laboratory conditions can be used with established relationships to predict cation concentrations in soil solutions associated with increased sulfate concentrations. However, using laboratory values in a Langmuir representation of sulfate absorption does not accurately simulate the time series of sulfate concentrations in these solutions.

## SECTION 3

## RECOMMENDATIONS

The effects of acid precipitation on forest soils can only be adequately studied in an ecosystem context. Specifically, the following must be considered:

1. Changes in rain chemistry caused by passage through canopy and litter layer.

2. Effects of altered soil solution chemistry on uptake of chemicals by plants.

3. Effects on other soil biological processes such as decomposition, nitrogen fixation, nitrification, sulfur oxidation/reduction, etc.

4. Effects on weathering of minerals.

5. Role of sulfate absorption by the soil in controlling the chemistry of the soil solution.

## SECTION 4

## EXPERIMENTAL PROCEDURES

Each of 18 lysimeter plots consisted of a 1.5 m x 1.5 m x 1.2 m watertight enclosure constructed of fiberglass covered plywood and filled to a depth of 1.1 m with a forest soil. The soil (Bohannon series of the fine-loamy, mixed, mesic family of Typic Halpumbrepts) was obtained from the Siuslaw National Forest, Oregon, and formerly had supported a red alder-Douglas-fir community. The horizons were reconstituted with respect to litter, topsoil, and subsoil layers. Each layer was mixed to minimize inter-plot differences. Soil properties are summarized in Table 1.

In 1975, 36 tree seedlings were planted in each system. Sugar maple (Acer saccharum) was planted in 9 of the plots, and red alder (Alnus rubra) in the other 9 plots. The model ecosystems also contained herbs and ferns brought in with the forest soil. Insects and tree frogs were observed on all plots. Each plot initially received litter obtained from natural tree stands of the corresponding species. Subsequently, leaf fall was collected from each plot and placed on the soil.

Each plot received simulated acid rain at one of four acidities, and each treatment was replicated. All plots received a stock solution approximating non-acidic rain containing 11 μeq/l $Ca^{++}$, 12 μeq/l $NH_4^+$, 5 μeq/l $Na^+$, 2 μeq/l $K^+$, 5 μeq/l $Mg^{++}$, 11 μeq/l $SO_4^{--}$, 12 μeq/l $NO_3^-$, and 12 μeq/l $Cl^-$. These concentrations were based on a seven year average from Hubbard Brook, New Hampshire,[42] after elimination of estimated sulfuric and nitric acid components. One set of four plots (two alder and two maple) served as controls, receiving only the stock solution equilibrated with atmospheric $CO_2$ to approximately pH 5.6. For three sets of four plots, sufficient $H_2SO_4$ was added to the stock solution to lower the pH to 4.0, 3.5, or 3.0. One plot on each end of the row of plots received only deionized water, and served as a buffer plot. Nozzles were used to apply simulated acid rain to the plots at the rate of 2.8 mm/hr (maple) or 3.7 mm/hr (alder) for 3 hours per day 3 days per week, throughout the year. Annual rain amounts (131 cm for maple and 173 cm for alder) approximated those of areas in which these species usually grow. Application of simulated acid rain began the last week of June, 1976. Rain was interrupted from December 6, 1977 to February 16, 1978 (32 rain events) due to winter damage to equipment. Severe freezing temperatures prevented nine rain applications during the winter of 1978-1979.

The plots were located under a transparent (90% transmittance) roof open on the ends and sides. Shade cloths were positioned over the plots during simulated rain events. The plots were thus subjected to ambient temperature, relative humidity, and light intensity except during simulated rain events. The facility is located on the Schmidt Research Farm of Oregon State University, near Corvallis, Oregon.

TABLE 1. CHEMICAL ANALYSES OF SOIL USED IN LYSIMETER STUDIES

| Level | Original Depth | Salts | Organic Matter | Total-N | $NO_3$-N | Zn | $SO_4$-S | P | K | Ca | Mg | Na | Cation Exchange Capacity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | cm | mmhos/cm | % | % | mg/kg | | | | | meq/100 g | | | |
| 1 | 0-20 | 0.22 | 11.1 | 0.30 | 15.4 | ---- | ---- | 10 | 204 | 1.0 | 0.43 | 0.07 | 31.5 |
| 2 | 20-40 | 0.28 | 8.1 | 0.24 | 24.1 | 0.25 | 7.8 | 7 | 254 | 2.2 | 0.93 | 0.17 | 33.0 |
| 3 | 40-50 | 0.20 | 8.1 | 0.26 | 16.9 | 0.14 | 7.4 | 5 | 218 | 0.9 | 0.40 | 0.12 | 37.7 |
| 4 | 50-60 | 0.13 | 3.9 | 0.15 | 11.1 | 0.09 | 12.0 | 4 | 138 | 0.6 | 0.40 | 0.10 | 30.7 |
| 5 | 60-110 | 0.10 | 2.0 | 0.08 | 4.1 | 0.09 | 20.4 | 3 | 114 | 0.6 | 0.74 | 0.11 | 30.6 |

Polypropylene beakers and funnels (Nalgene) were used to sample rain and throughfall bi-weekly for chemical analysis. Ceramic candles (Soil Moisture Equipment Corp.) were joined to form 1.3 m tubes; seven such tubes were placed parallel to each other 10 cm above the bottom of each plot (100 cm below the soil surface) and connected to a five-gallon glass carboy (Kimble) above the soil. Two 30 cm ceramic candles were placed 23 cm below the soil surface (Level 2 in Table 1) and connected to a 500 ml polypropylene filtering flask (Nalgene); after the soil settled, these were approximately 20 cm below the surface. Porous ceramic disks (Coors) were cemented to polypropylene funnels (Nalgene). These were placed so that the ceramic disks were slightly above the soil surface in the litter layer, and the funnels were connected to 500 ml polypropylene filtering flasks (Nalgene). In all cases, tubing and fittings were polypropylene and stoppers were Vikem (Belart). Litter leachate and 20-cm soil solution were sampled bi-weekly for chemical analysis by applying vacuum to the filtering flasks. To prevent soil saturation, vacuum was applied to the ceramic at 100 cm depth whenever water could be drawn from the soil; this solution was sampled for chemical analysis every four weeks. Water samples were analyzed for pH, $Ca^{++}$, $Mg^{++}$, $SO_4^{=}$, and $NO_3^{-}$.

## SECTION 5

## RESULTS

Changes in chemical content of water after percolation through various layers are summarized in Figures 1 through 17. Throughout this set of figures, the same set of symbols is used to indicate the four rain pH treatments. On several figures, a diagonal line indicates points at which concentrations at two locations within a plot (e.g. rain and throughfall) would be equal. There are 150 to 160 points for each rain treatment on each figure, for an approximate total of 600 points per figure. In many cases, results from the control plots fell over an extremely narrow range. Thus, what appears as a single plus (+) in the lower left of the figures frequently represents many independent measurements.

### THROUGHFALL

Figure 1 shows pH and Figure 2 sulfate concentration of throughfall versus pH of rain. For both pH and sulfate, results fell close to the line of equality for both alder (1a, 2a) and maple (1b, 2b).

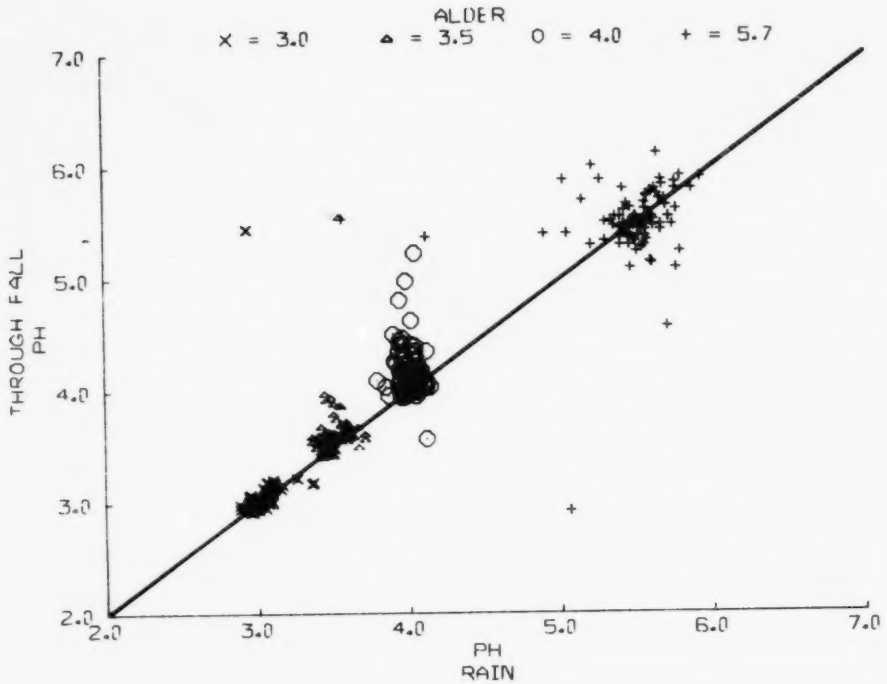
Figure 3 shows magnesium concentration and Figure 4 calcium concentration versus sulfate concentration in throughfall. Little if any tendency towards increased leaching of either cation with increased sulfate concentration is evident for alder (3a, 4a) or maple (3b, 4b).

### LITTER LEACHATE

The pH of water that had percolated through the litter is plotted against the pH of the incident rainwater in Figure 5. For all sulfuric acid treatments, the pH of the litter leachate was considerably higher than the pH of the incident rain, indicating partial neutralization of the acid by the litter. This effect was stronger for alder litter (5a) than for maple litter (5b), to the point that no difference in the pH of the litter leachate was apparent between alder plots receiving either pH 4.0 or control rain. For plots receiving control rain, the pH of the litter leachate typically was somewhat less than the pH of the rain for alder and somewhat higher for maple.

The concentrations of sulfate in litter leachate and in rain are compared in Figure 6. For both alder (6a) and maple (6b) the concentration was generally greater in the litter leachate than in the corresponding acid rain. This tendency was most pronounced for maple, especially for the pH 3.0 rain treatment.

A.




B.

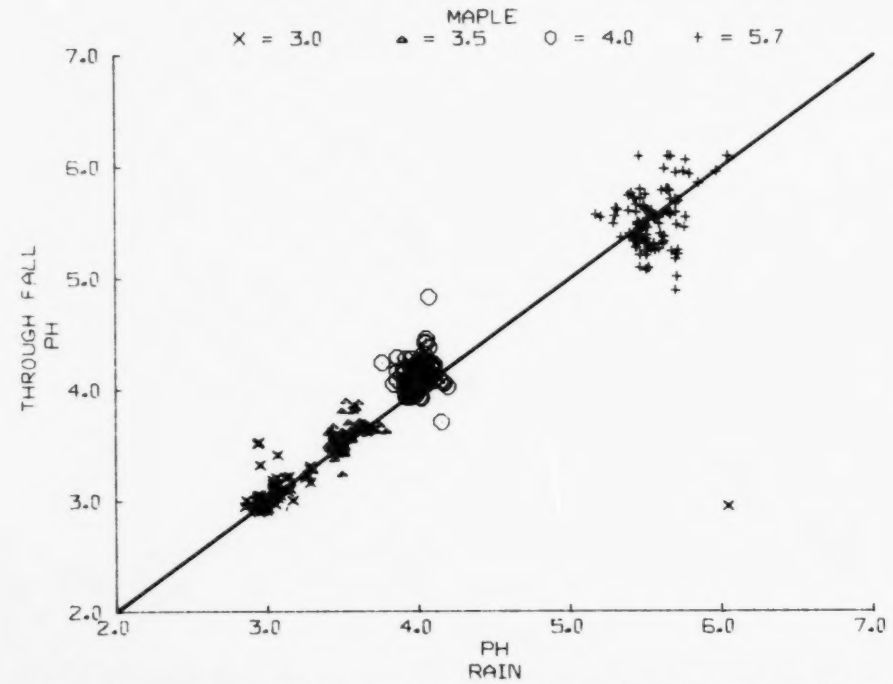
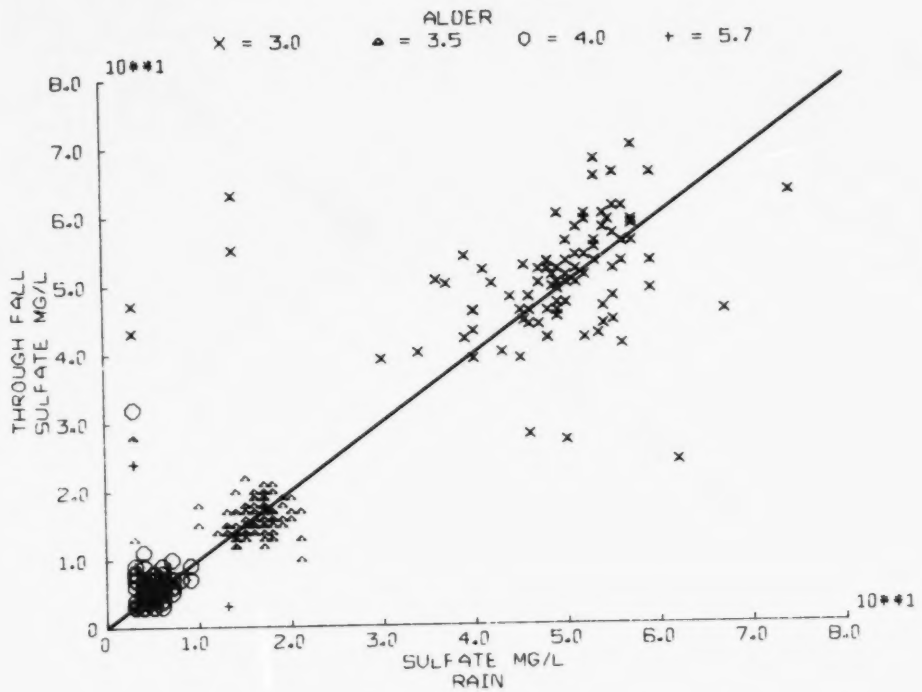



Figure 1. pH of throughfall vs. pH of rain. Symbols refer to nominal pH of rain treatment. Diagonal line represents points at which rain and throughfall pH values would be equal.

A.




B.

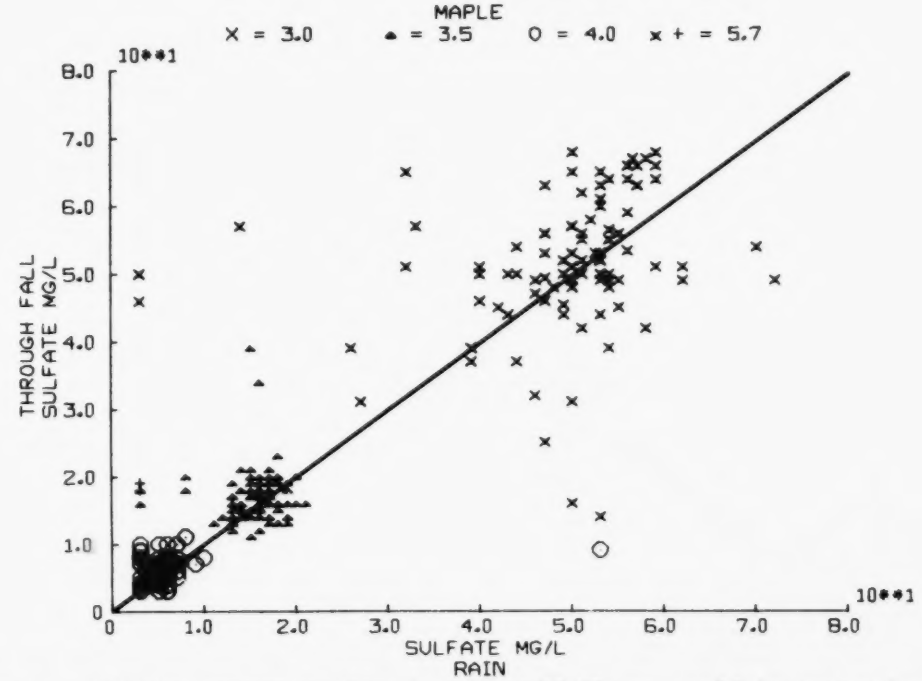
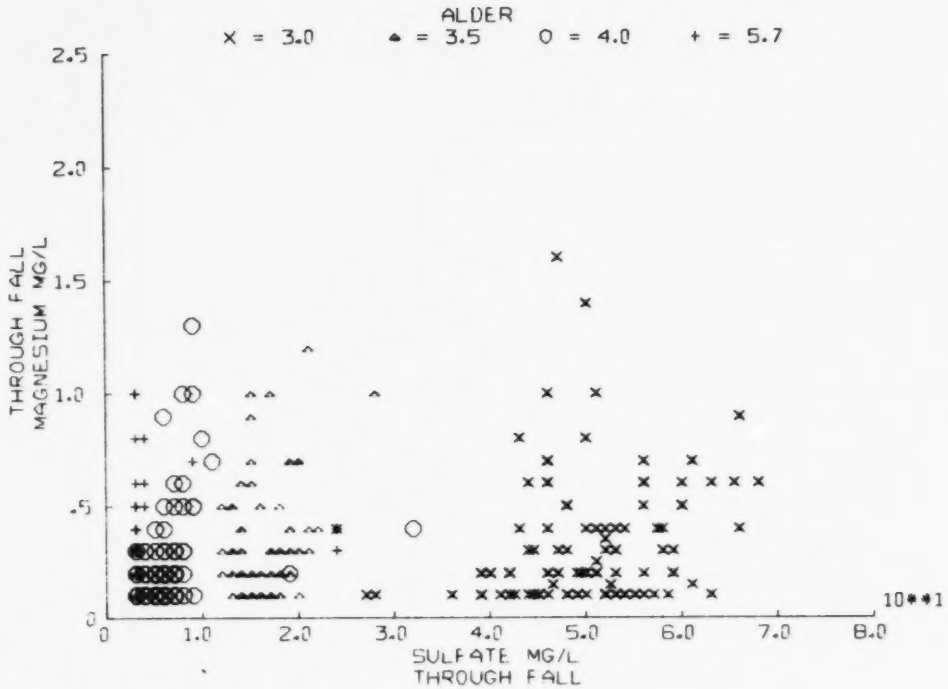



Figure 2. Sulfate concentration in throughfall vs. sulfate concentration in rain. Symbols refer to nominal pH of rain treatment. Diagonal line represents points at which rain and throughfall sulfate concentrations would be equal.

A.

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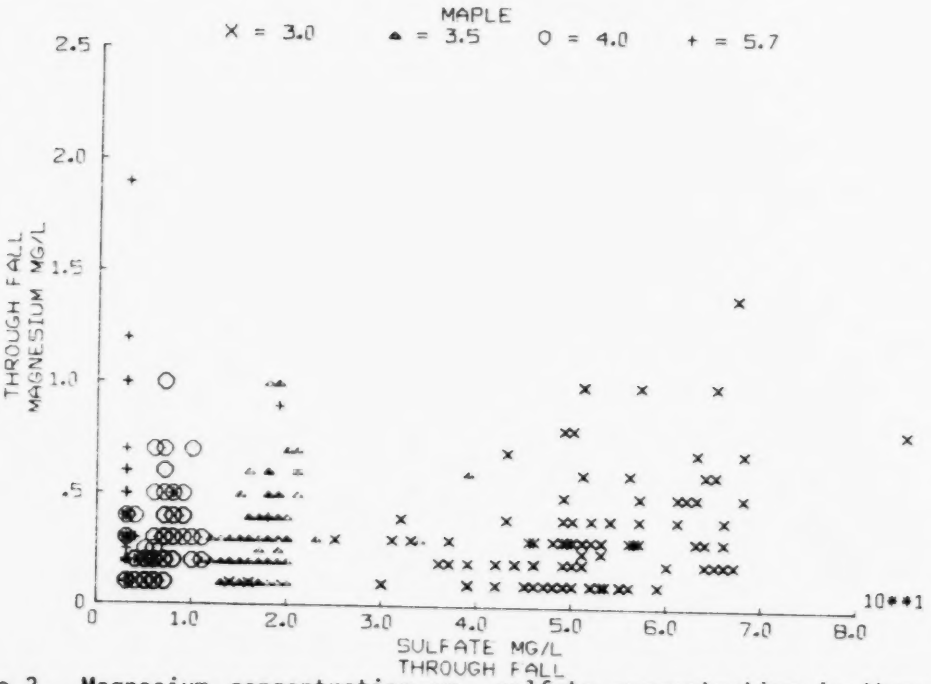
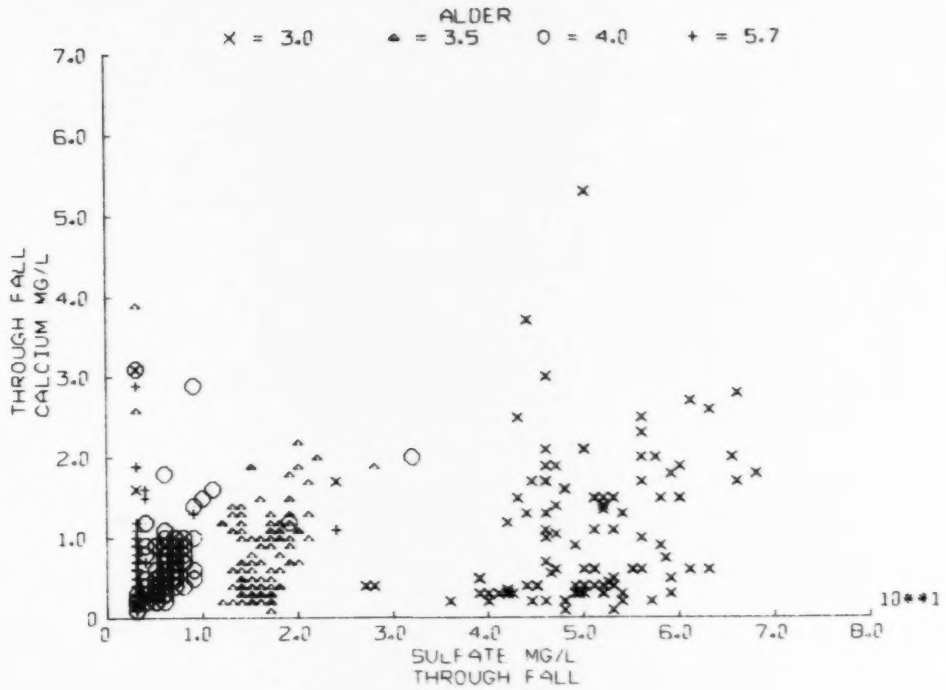



Figure 3. Magnesium concentration vs. sulfate concentration in throughfall. Symbols refer to nominal pH value of rain treatment.

A.




B.

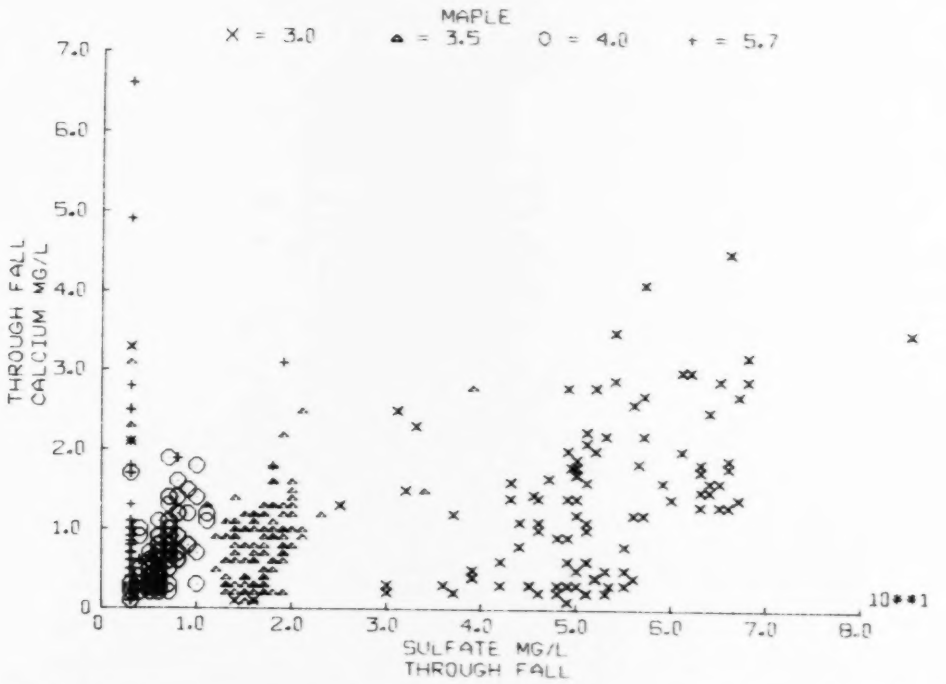



Figure 4. Calcium concentration vs. sulfate concentration in throughfall. Symbols refer to nominal pH value of rain treatment.

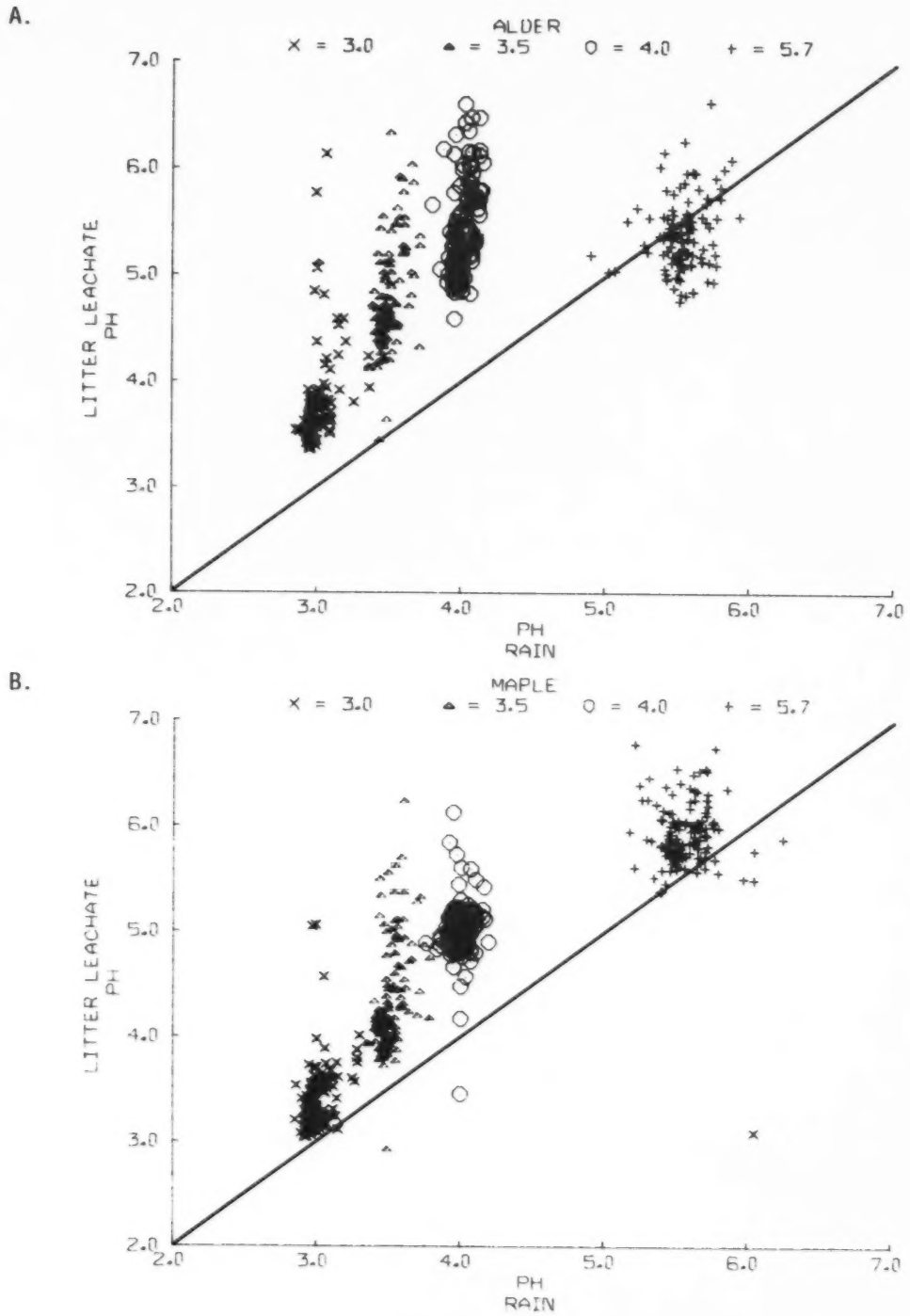



Figure 5. pH of litter leachate vs. pH of rain. Symbols refer to nominal pH value of rain treatment. Diagonal line represents points at which pH values of rain and litter leachate would be equal.

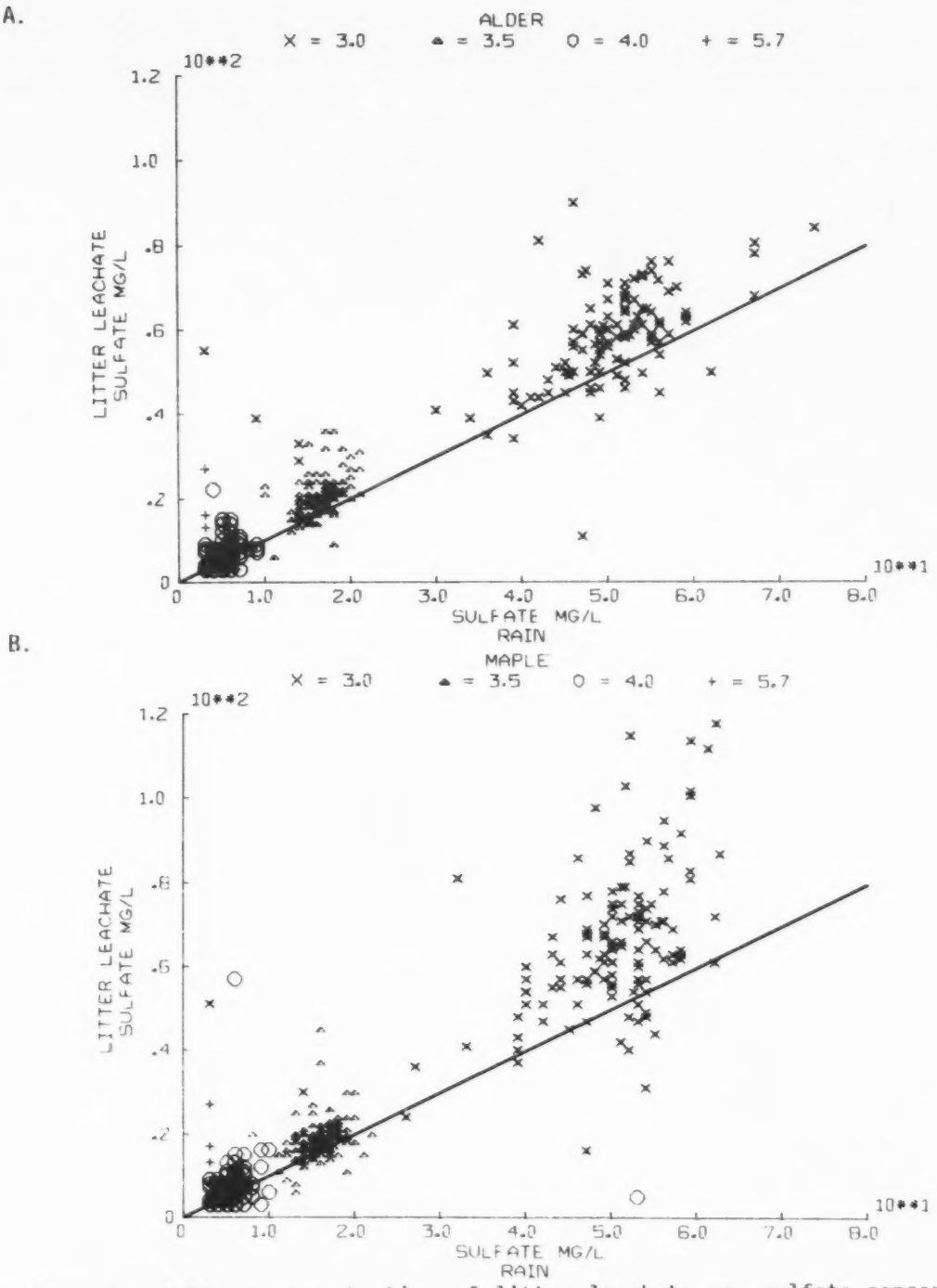



Figure 6. Sulfate concentration of litter leachate vs. sulfate concentration of rain. Symbols refer to nominal pH value of rain treatment. Diagonal line represents points at which sulfate concentrations of rain and litter leachate would be equal.

The variation of magnesium with sulfate in litter leachate is shown in Figure 7; Figure 8 shows this variation for calcium. Although the data points shown in Figures 7 and 8 were scattered, there was an apparent tendency towards increased leaching of calcium from the maple litter layer with increased sulfate concentrations (Figure 8b).

## TWENTY-CENTIMETER SOIL SOLUTION

Figures 9 through 12 show the time series of sulfate, magnesium, calcium, and pH in solution 20 cm below the soil surface. Week one, the last week in June, 1976, was the first week in which the plots received acid rain. During week zero, all plots received control rain.

For the first six months, there were no apparent differences in sulfate (9b), magnesium (10b), or calcium (11b) concentrations in 20-cm soil solutions from maple plots receiving acid rain or control treatments. At that time, sulfate concentrations for plots receiving the most acid rain (pH 3.0) became increasingly higher than for the other plots. After three years, sulfate concentrations in the 20-cm soil solution became approximately equal to the concentrations in the rain. Solutions corresponding to the pH 3.5 and pH 4.0 treatments responded similarly starting one year and two years, respectively, after the initiation of simulated acid rain exposures. Magnesium (10b) and calcium (11b) concentrations generally followed the sulfate trend. Figures 13b and 14b show the relation between sulfate concentrations and the concentrations of magnesium and calcium; the curves are "eyeball fits" to the data. Magnesium and calcium concentrations followed similar trends (16b).

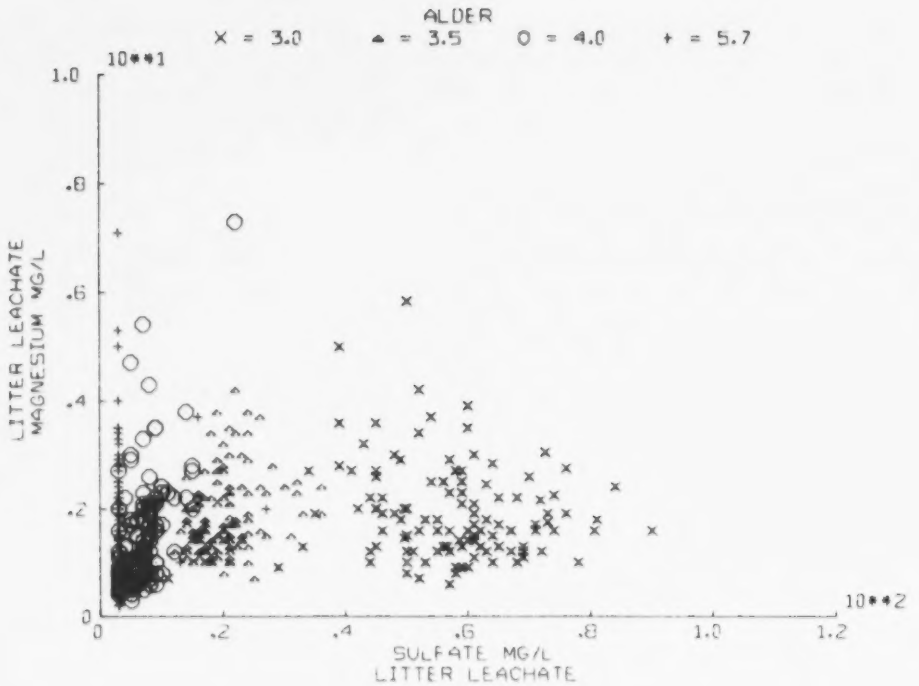
Dry soil conditions prevented extraction of 20-cm soil solution samples from the alder plots during the early part of the experiment. For the period for which samples were taken, the patterns for alder (Figures 9a, 10a, 11a, 13a, 14a, 16a) were similar to those for maple. There was, however, greater scatter of the data points, and, especially for magnesium (10a), an indication of seasonal trends.

The pH of the 20-cm soil solution followed a trend towards lower values for both alder (12a) and maple (12b) plots for all treatments. The lower pH values were often associated with with higher sulfate concentrations (15a, 15b).

## ONE-METER SOLUTION

The pH values of soil solutions at a depth of one meter did not vary greatly during 3.5 years (Figure 17). For all plots, sulfate concentrations were generally below the sensitivity of the analytical method (3 mg/l).

A.




B.

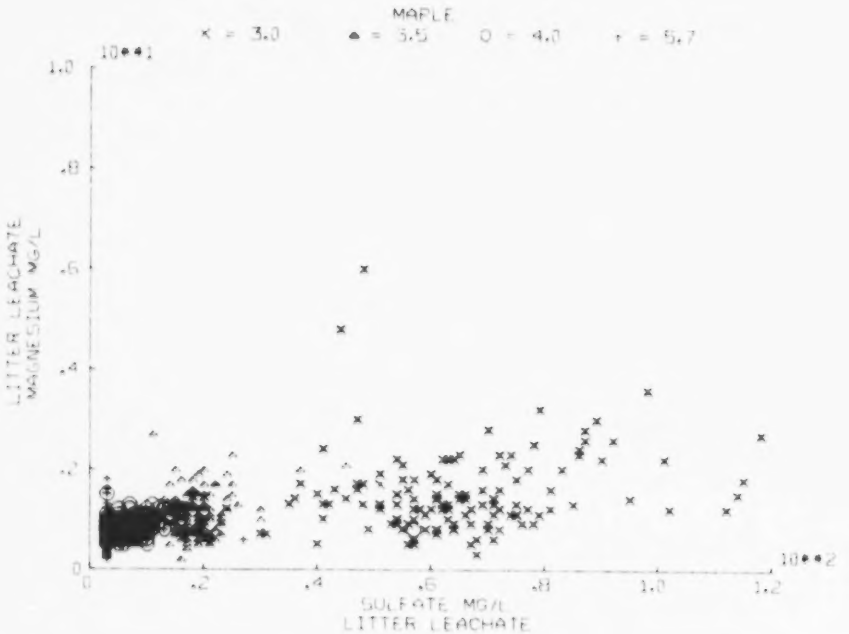
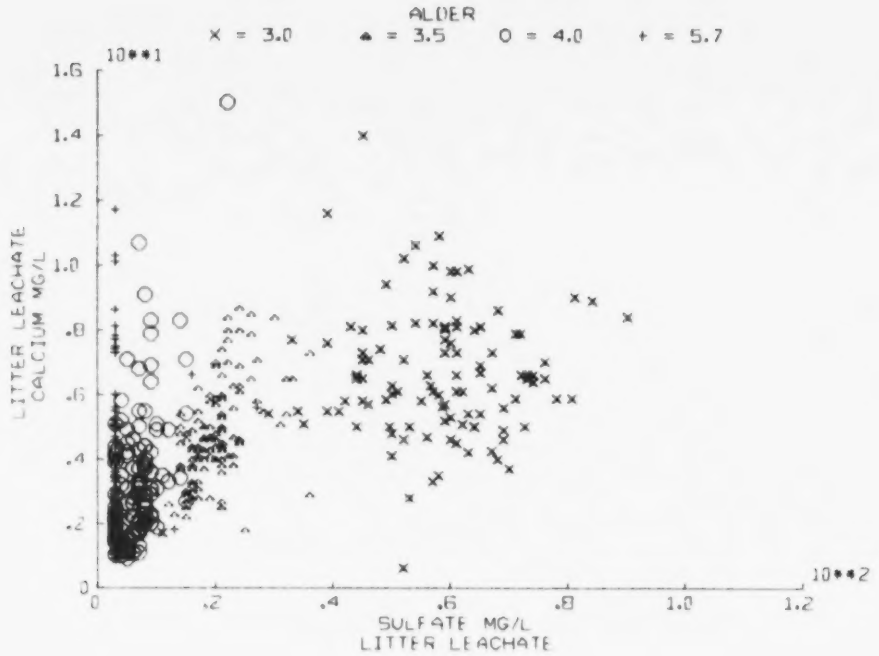



Figure 7. Magnesium concentration vs. sulfate concentration of litter leachate. Symbols refer to nominal pH value of rain treatment.

A.




B.

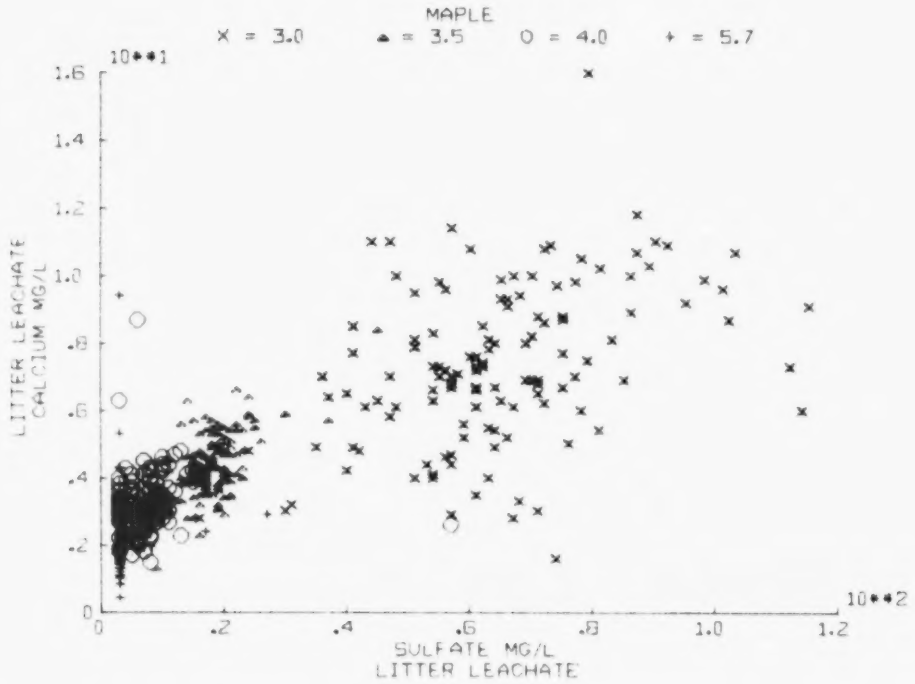
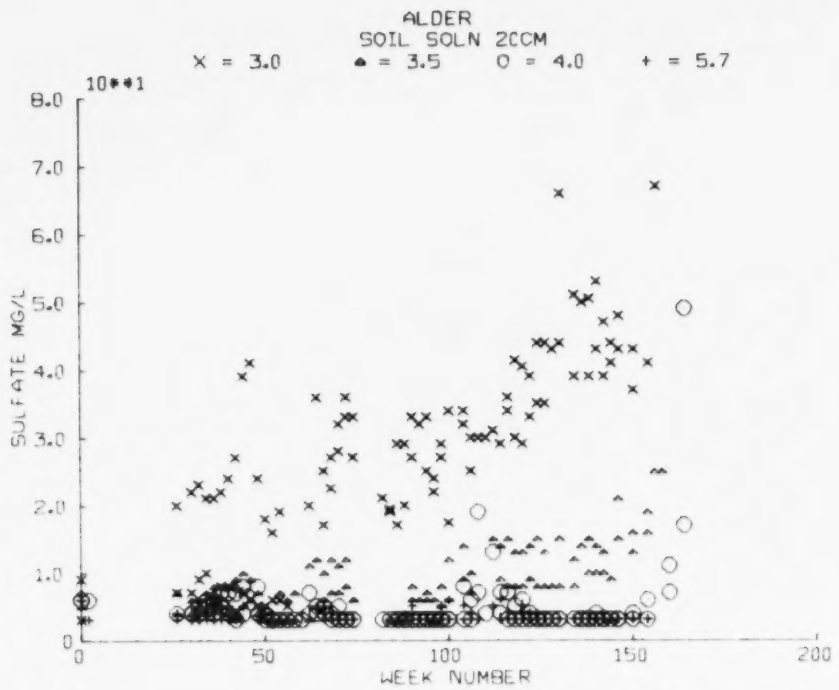



Figure 8. Calcium concentration vs. sulfate concentration of litter leachate. Symbols refer to nominal pH value of rain treatment.

A.




B.

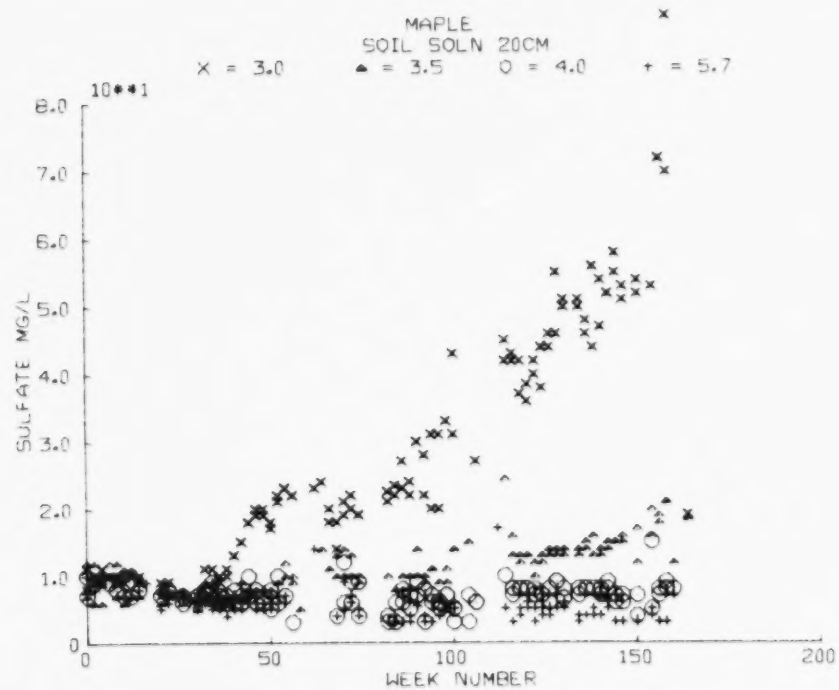
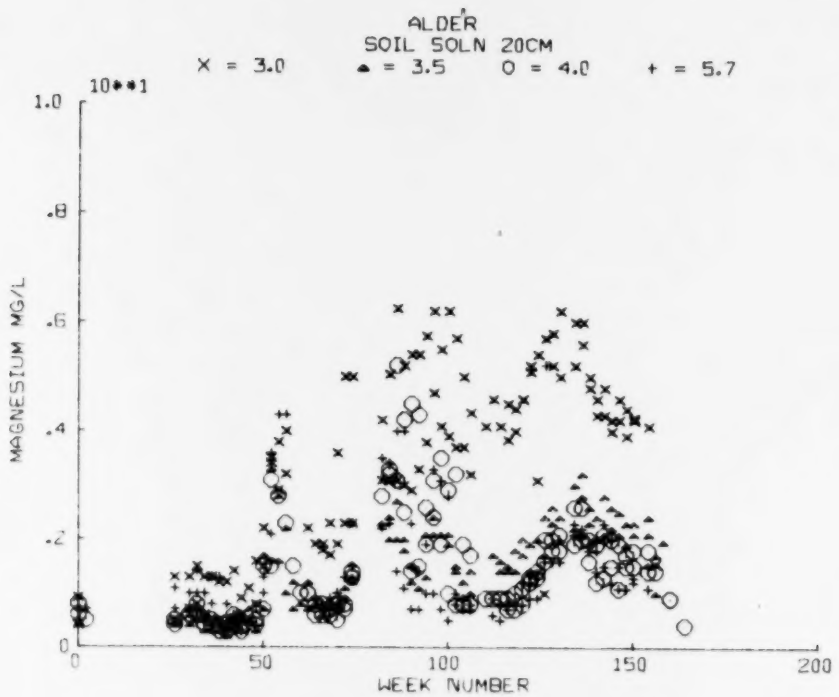



Figure 9. Sulfate concentration of 20-cm soil solution vs. time since beginning of treatment. Symbols refer to nominal pH value of rain treatment.

A.




B.

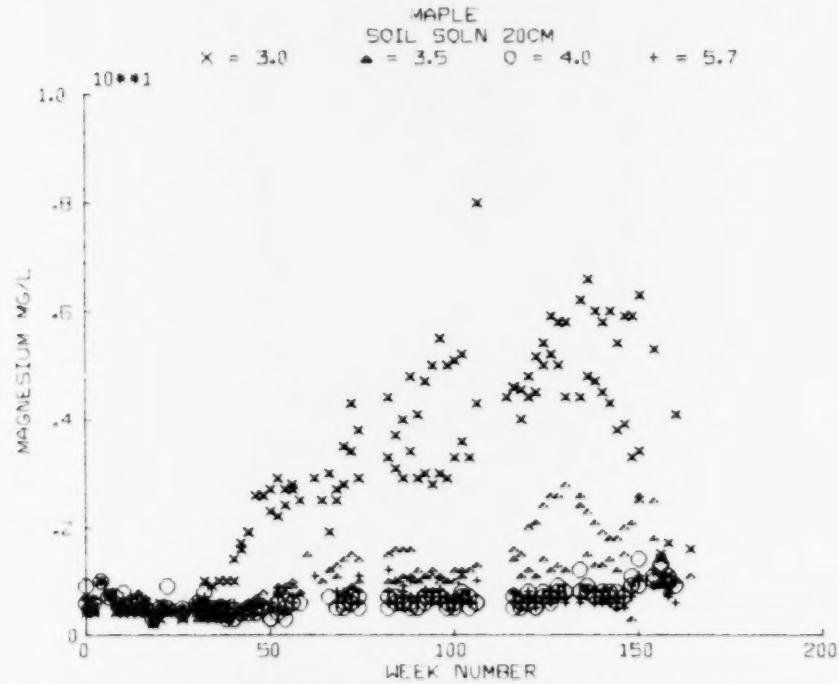
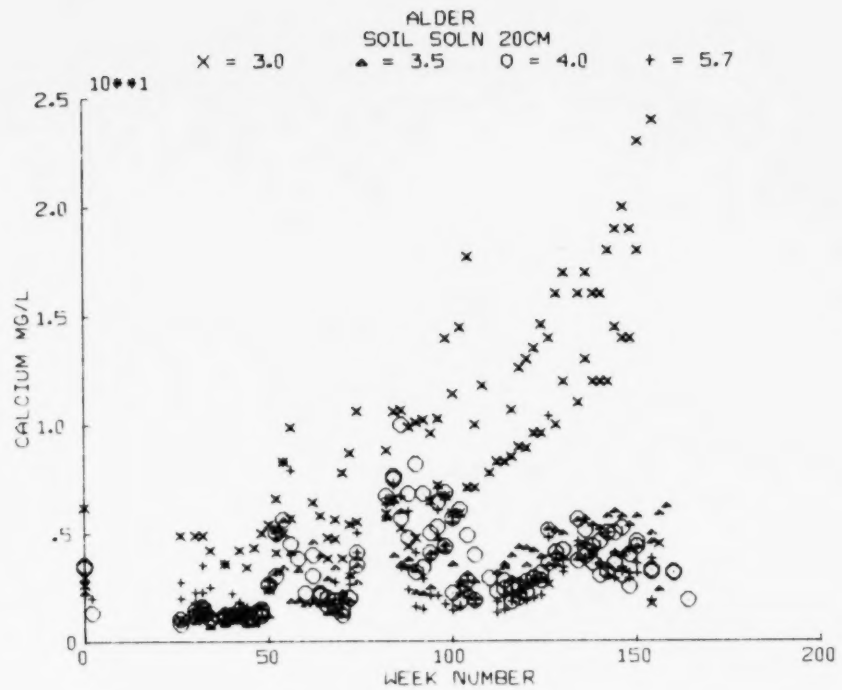



Figure 10. Magnesium concentration of 20-cm soil solution vs. time since beginning of treatment. Symbols refer to nominal pH value of rain treatment.

A.




B.

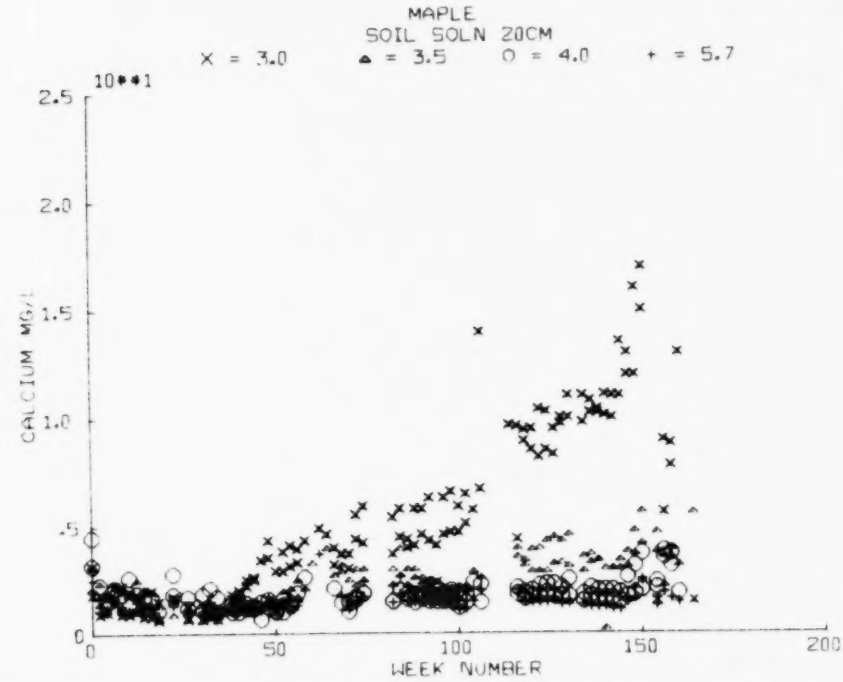
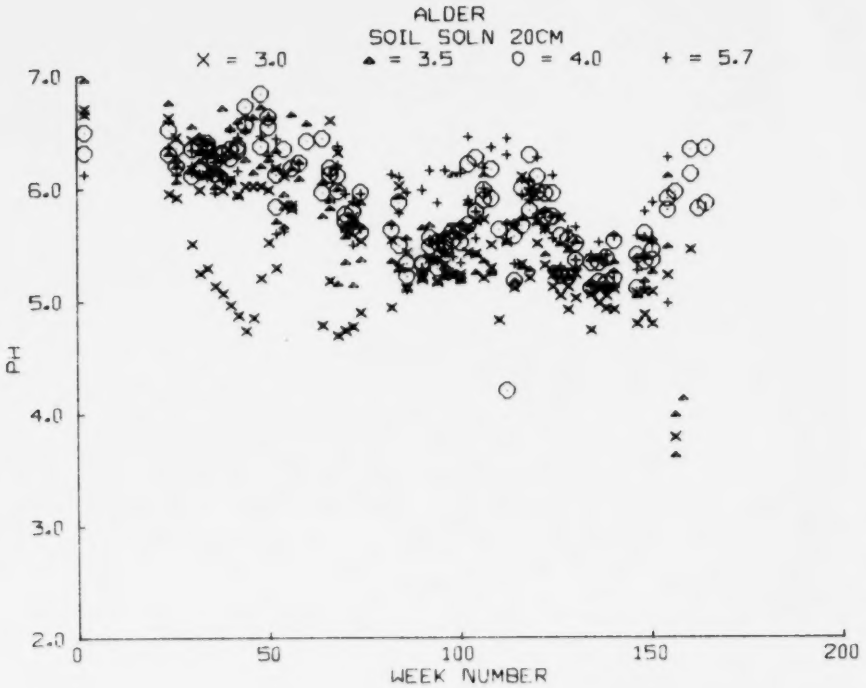



Figure 11. Calcium concentration of 20-cm soil solution vs. time since beginning of treatment. Symbols refer to nominal pH value of rain treatment.

A.




B.

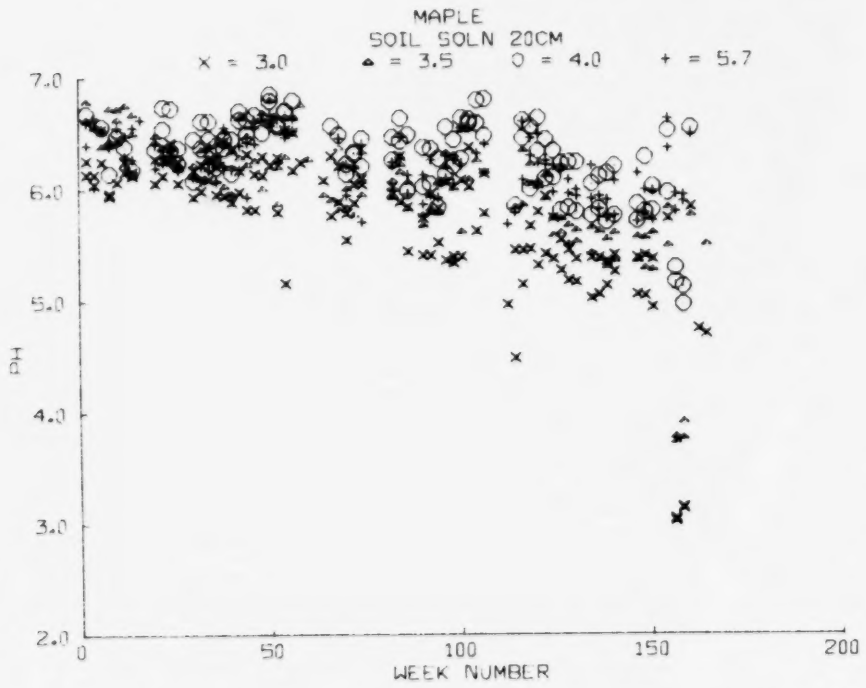



Figure 12. pH of 20-cm soil solution vs. time since beginning of treatment. Symbols refer to nominal pH value of rain treatment.

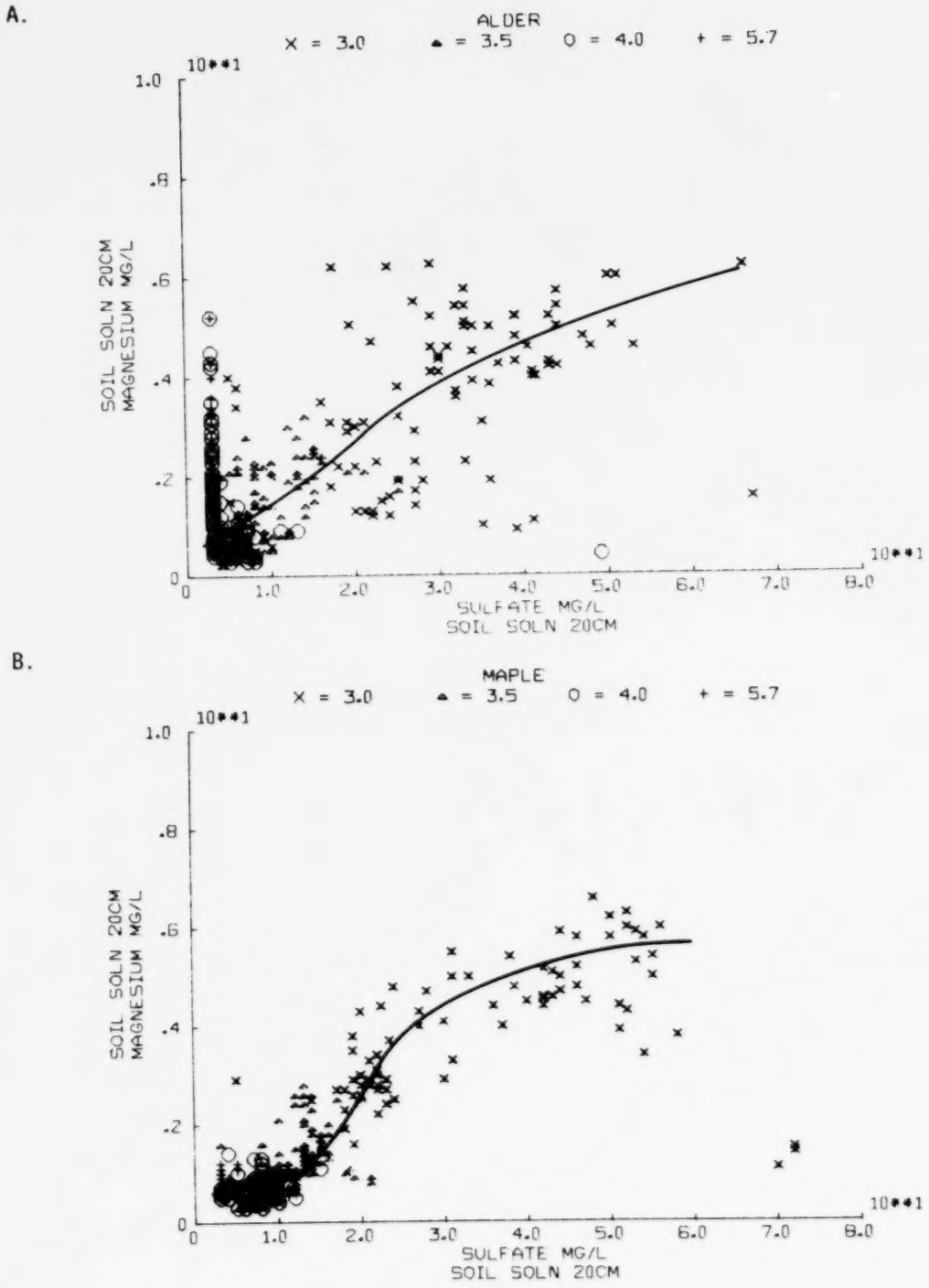
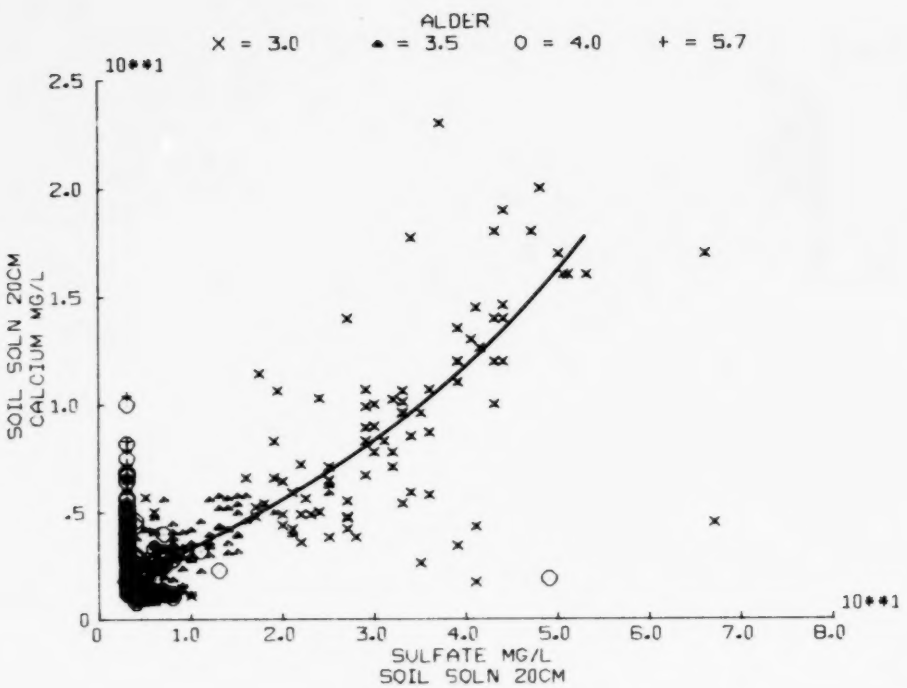



Figure 13. Magnesium concentration vs. sulfate concentration of 20-cm soil solution. Symbols refer to nominal pH value of rain treatment.

A.




B.

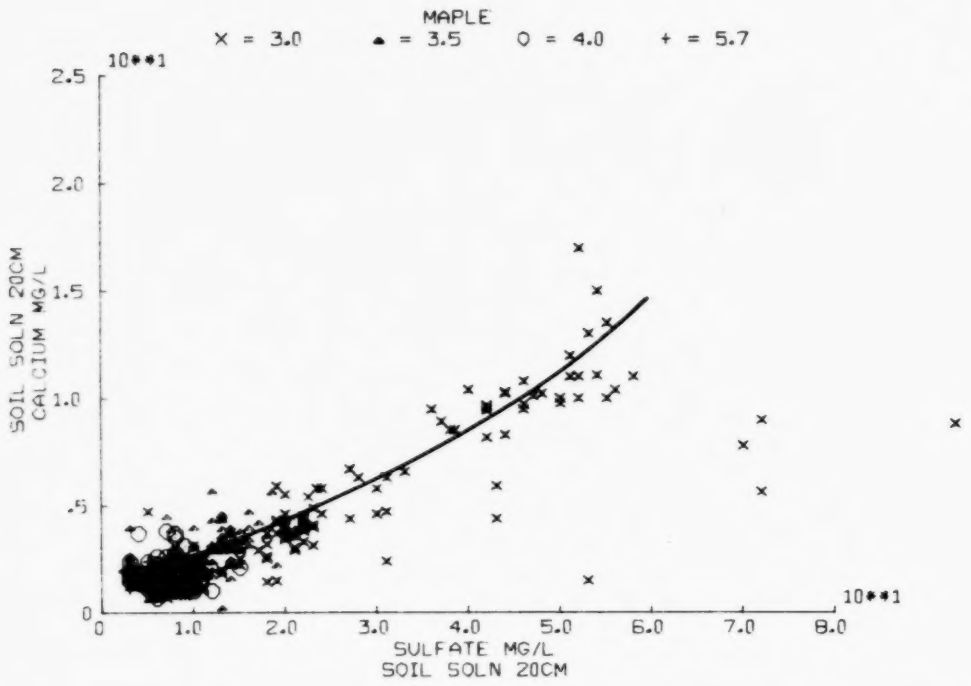
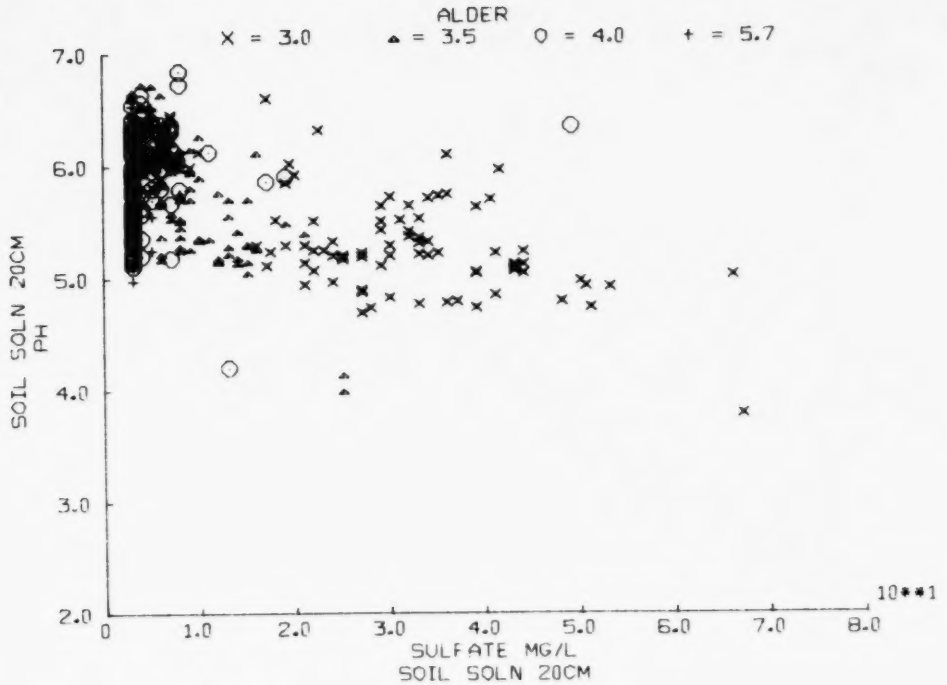



Figure 14. Calcium concentration vs. sulfate concentration of 20-cm soil solution. Symbols refer to nominal pH value of rain treatment.

A.




B.

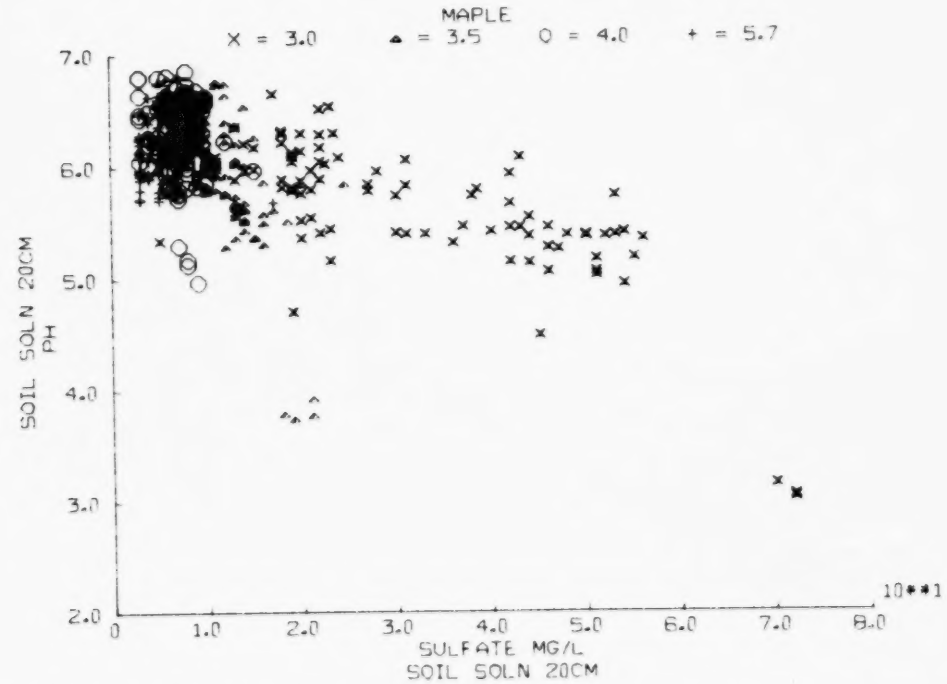
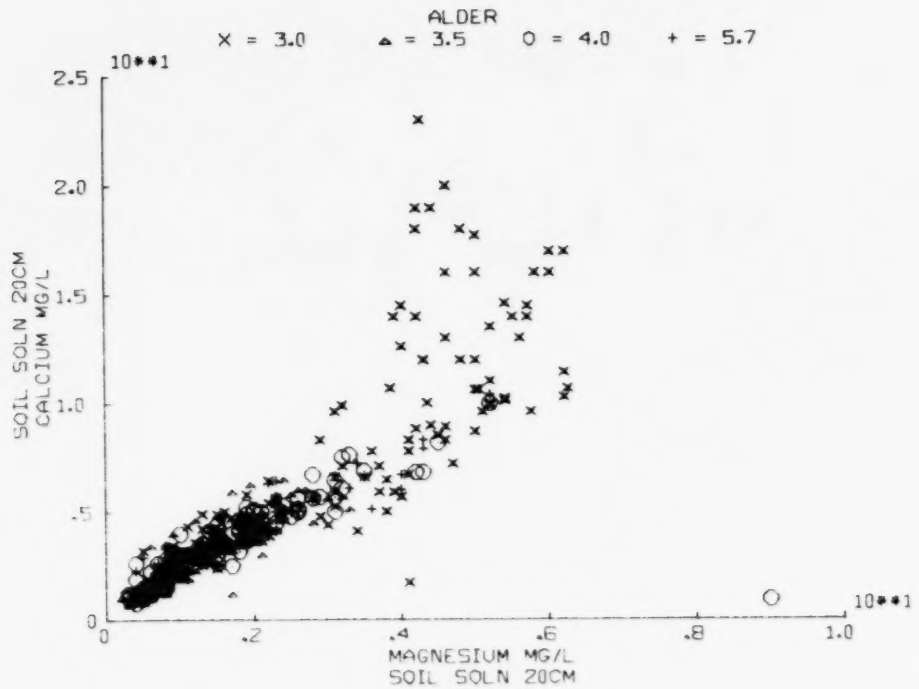



Figure 15. pH vs. sulfate concentration of 20-cm soil solution. Symbols refer to nominal pH value of rain treatment.

A.




B.

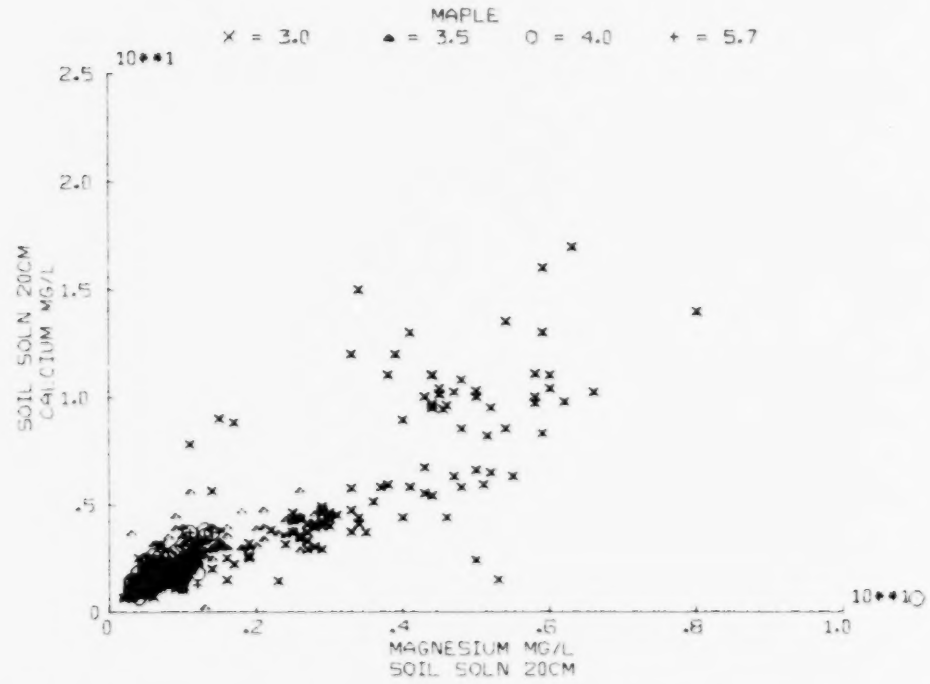
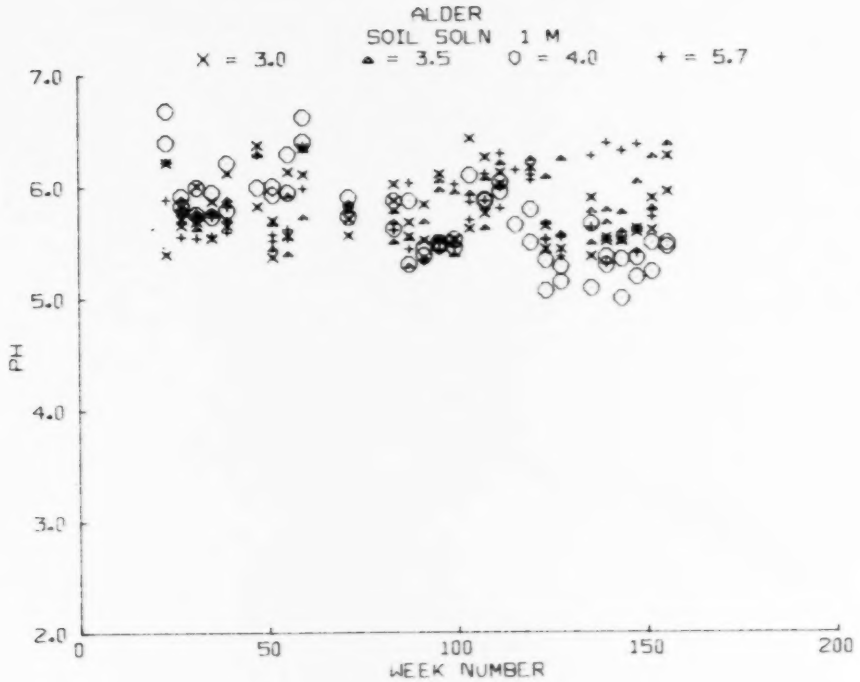



Figure 16. Calcium concentration vs. magnesium concentration of 20-cm soil solution. Symbols refer to nominal pH value of rain treatment.

A.




B.

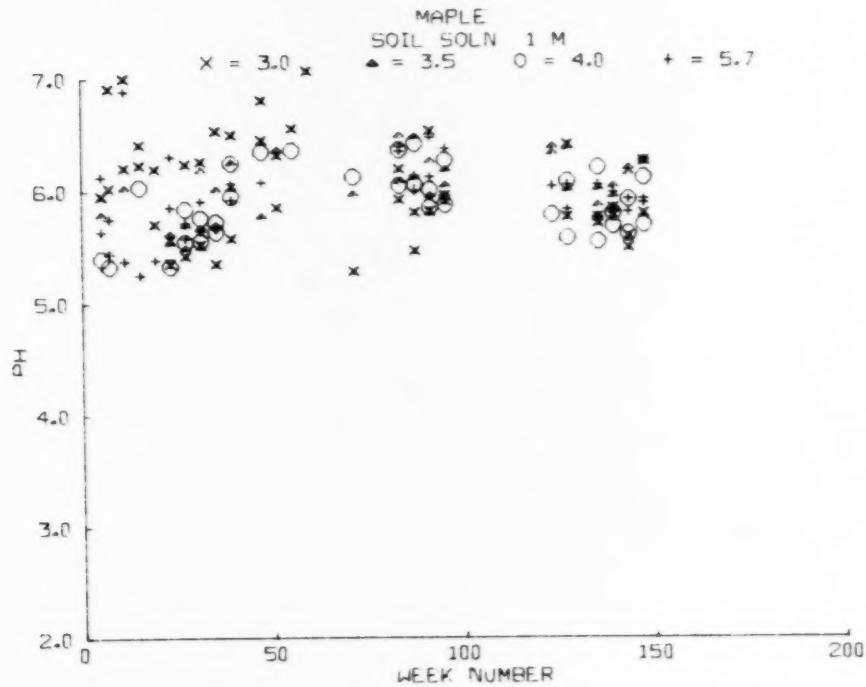



Figure 17. pH of 1-m soil solution vs. time since beginning of treatment. Symbols refer to nominal pH value of rain treatment.

## SECTION 6

## DISCUSSION

Eaton et al.[35] determined throughfall chemistry in a sugar maple stand receiving ambient acid rain (pH 4.1). Their results for $Ca^{++}$, $Mg^{++}$, and $SO_4^{--}$, summarized in Table 2, indicated that partial neutralization occurred in the canopy, and that throughfall was considerably enriched in $Ca^{++}$, $Mg^{++}$, and $SO_4^{--}$, compared to incident precipitation. These effects were more pronounced for trees with 40-65 cm dbh (diameter breast height) than for trees with 15-25 cm dbh. Our results for small maple trees (less than 5 cm dbh) exposed to simulated sulfuric acid rain at pH 4.0 were similar to theirs; however, we did not observed increases in sulfate concentration caused by passage of rainwater through the canopy.

When Fairfax and Lepp[39] exposed maple (Acer pseudoplatanus) leaf litter to simulated sulfuric acid rain at pH 4.0, the resultant leachate had a pH of 5.2. Calcium concentration in this leachate was 13 times that in leachate from litter exposed to deionized water (pH 6.8); similar results were obtained for the other hardwood litters they tested. We also found significant neutralization of sulfuric acid by litter (Figure 5), and that, for maple litter, higher calcium concentrations (Figure 8b) were associated with the more acidic treatments. Thus, when acid rain falls on a hardwood forest with a well developed canopy and litter layer, the actual input to the soil will probably be considerably less acid than the incident precipitation. Also, precipitation which is more acid will cause more rapid leaching of cations into the soil. These effects could, for at least a few years, tend to offset any leaching of cations from the soil.

Cronan et al.[43] observed average sulfate concentrations of 8 mg/l in soil solutions beneath a coniferous forest in New England; they attributed 76% of cation leaching from the soil to the presence of sulfate anion. For solutions obtained from beneath a hardwood forest subject to acid rain, Koterba et al.[44] observed an average sulfate concentrations of 5 mg/l. In both cases, the soils had been exposed to sulfuric acid rain for approximately 30 years, and to non-acidic sulfate rain for considerably longer. The ability of the soil to absorb sulfate probably has been exhausted in that area. While soil solutions in areas which have only recently begun to receive sulfuric acid rain might not show an immediate response to increased sulfate loadings, the response to nitric acid rain would be more rapid.[16,17,45]

The soil used in our experiment was a strong sulfate absorber.[16] Figure 9b demonstrates a breakthrough phenomenon as the sulfate absorption capacity of the soil was approached. As expected from the theoretical work of Wiklander,[14,15] Johnson and Cole,[16] and Reuss,[17] increased anion concentrations caused increased concentrations of $Ca^{++}$ and $Mg^{++}$ and lowered pH in the

TABLE 2. CHEMICAL CONTENT OF PRECIPITATION AND THROUGHFALL IN A SUGAR MAPLE STAND

| | Precipitation | Throughfall | |
|---|---|---|---|
| | | Small Trees* | Large Trees* |
| $Ca^{++}$ | 0.16 mg/l | 1.13 mg/l | 1.58 mg/l |
| $Mg^{++}$ | 0.03 | 0.37 | 0.40 |
| $SO_4^{--}$ | 2.7 | 16.4 | 25.2 |
| pH | 4.1 | 4.6 | 4.9 |

* 15-24 cm dbh.
** 40-65 cm dbh.

Adapted from Eaton et al.[35]

soil solutions (Figures 13-15). These changes were not necessarily due to changes in the base saturation of the soil, but were probably the result of increased ionic strength of the soil solution. The increased scatter of data on cation concentrations for alder plots was probably due to variable $NO_3^-$ concentrations associated with symbiotic nitrogen fixation, a characteristic of the genus Alnus. Although the "sulfate front" presumably has moved downwards into the soil, it has not reached a depth of 1 m; no effects attributable to acid rain were observed in solutions extracted from this depth.

To better compare the data with theoretical predictions, the expected response of soil solution chemistry to acid rain was simulated using the LEACH computer model.[17,41] Given the temporal pattern of chemical content and amount of rain, this model uses established soil chemistry relationships to predict the time series of soil solution concentrations of $H^+$, $Ca^{++}$, $Al^{3+}$, $SO_4^=$, $Cl^-$, and $HCO_3^-$ in non-calcareous, acid soils. In this model, calcium may be considered to be a proxy for other cations, and chloride a proxy for other anions. The model uses the Langmuir equation for the relationship between absorbed sulfate, $S_a$, and sulfate in solution, $S_s$,

$$S_a = \frac{SMAX \cdot S_s}{SKLR + S_s},$$

where $S_a$ is in moles/kg soil and $S_s$ is in moles/l. SMAX and SKLR are constants determined from laboratory data.

While evapotranspiration effects are considered, the model does not take into account the weathering of minerals by acids, uptake of nutrients by plants, or microbial alteration of chemical species.

Soil parameters used for these simulations are listed in Table 3a. Soil solution data obtained shortly after the start of the experiment were used to estimate the initial value of the non-sulfate anion content of the soil and to translate the lime potential (LP) vs. base saturation (BS) curve for non-montmorillonitic soils[17] to pass through the point LP = 3.15, BS = 0.10. All other soil parameters were those obtained from results of laboratory analyses, including those listed under "Level 2" of Table 1. Evapotranspiration rates (Table 3b) were adjusted so that predicted values of soil water content were consistent with the rates at which water was extracted from the plots.

The chemical composition of the simulated "rains" (Table 3d) approximated those values observed for the litter leachate. The volume of rain (Table 3c) was set equal to the amount of throughfall for each month, and was somewhat less than the amount of rain applied to the experimental plots.

The simulated time series of sulfate concentrations in the maple plots is shown in Figure 18. Observed sulfate concentrations (Figure 9b) increased considerably faster than predicted by the model. For example, for the pH 3.0 treatment the model predicts that a concentration of 40 mg/l would be reached only after 10 years; this concentration was actually reached in approximately 2 years. Thus, either the Langmuir parameters obtained under laboratory conditions were not relevant to field conditions, or the Langmuir formulation may not be an appropriate representation of sulfate absorption by this soil.

TABLE 3. PARAMETERS USED IN LEACH SOIL SOLUTION SIMULATION MODEL

3A. Soil Parameters

| | |
|---|---|
| Thickness | 20.3 cm |
| Bulk Density | 0.84 kg/l |
| Field Capacity | 0.382 l $H_2O$/l soil |
| Wilting Point | 0.193 l $H_2O$/l soil |
| Cation Exchange Capacity | 56.2 equiv/$m^2$ |
| Total Calcium* | 3.350 moles/$m^2$ |
| Total Sulfate | 0.042 moles/$m^2$ |
| Total Chloride** | 0.004 moles/$m^2$ |
| Partial Pressure $CO_2$ | 0.001 atmosphere |
| Sulfate Absorption: (see text) | |
| SMAX | 0.811 x $10^{-2}$ moles/kg soil |
| SKLR | 0.800 x $10^{-3}$ moles/l |

* Represents all bases.
** Represents all anions except sulfate.

3B. Daily Evapotranspiration (mm $H_2O$)

| | July | Aug | Sept | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | June |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alder | 0.49 | 0.43 | 0.29 | 0.08 | 0.05 | 0.04 | 0.04 | 0.07 | 0.09 | 0.28 | 0.31 | 0.41 |
| Maple | 0.44 | 0.38 | 0.22 | 0.06 | 0.04 | 0.03 | 0.03 | 0.05 | 0.08 | 0.16 | 0.23 | 0.36 |

3C. Rainfall Rate (cm/rain event)

| | July | Aug | Sept | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | June |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alder | 0.7 | 0.6 | 0.7 | 0.8 | 0.9 | 1.1 | 1.0 | 1.0 | 1.0 | 1.0 | 0.9 | 0.8 |
| Maple | 0.5 | 0.6 | 0.6 | 0.7 | 0.9 | 1.0 | 0.9 | 0.8 | 0.8 | 0.7 | 0.6 | 0.5 |

3D. Chemical Composition of Rain

| Nominal pH | Solution pH | $Ca^{++}+Mg^{++}$ | $SO_4^{--}$ |
|---|---|---|---|
| | | $10^{-5}$ moles/l | |
| 5.6 | (5.6) | 1.75 | 0.55 |
| 4.0 | 4.4 | 4.76 | 5.55 |
| 3.5 | 3.8 | 9.64 | 32.17 |
| 3.0 | 3.1 | 12.03 | 50.60 |

3E. Chloride + Nitrate Content of Rain ($10^{-5}$ moles/l)

| | July | Aug | Sept | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | June |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alder | 19.1 | 2.99 | 10.1 | 15.5 | 19.1 | 22.6 | 28.0 | 29.8 | 31.6 | 31.6 | 29.8 | 28.0 |
| Maple | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 |

The simulated relationship between sulfate concentration and calcium concentration for the maple plots is shown in Figure 19a. Four points obtained by summing calcium and magnesium concentrations from the curves in Figures 13b and 14b are also shown. The predicted and observed relationships are quite similar.

An attempt was made to simulate the effects of nitrogen fixation in the alder plots by introducing a seasonal variation in the anionic content (represented by $Cl^-$) of the simulated rain (Table 3e). This induced a seasonal variation in anionic concentration of the simulated soil solution similar to that observed in extracts from the alder plots, but with higher average anionic content. This caused the predicted concentrations of Ca and Mg to be higher than the observed concentrations (Figure 19b). The variability of simulated anion concentrations caused the results to be more scattered for alder (Figure 19b) than for maple (Figure 19a); this same tendency was observed in the data (Figures 13a and 14a vs. Figures 13b and 14b).

The simulation results demonstrate that established relationships can be used to predict the response of cations in soil solutions to increased loading of anions due to acid rain. In particular, the LEACH model is an adequate representation of those relationships. Future efforts need to focus on simulating sulfate concentrations more closely. Mineral weathering and plant uptake of nutrients also need to be considered.

According to the LEACH simulations, the changes in soil solution chemistry (increased calcium and magnesium concentrations, lowered pH) were almost entirely due to increases in total anion concentration rather than to changes in base saturation. An example is the simulation summarized in Table 4. While the predicted pH of the soil solution dropped from 5.3 to 4.9, base saturation was virtually unchanged. The change in pH was associated with the change in sulfate concentration. The dependence of the pH of a solution in equilibrium with soil on the ionic strength of the equilibrating solution is well known to those routinely performing soil analyses. These results emphasize the need to distinguish between acidification of soil solution, on the one hand, and acidification of soil as measured by decreases in base saturation.[14,15,17]

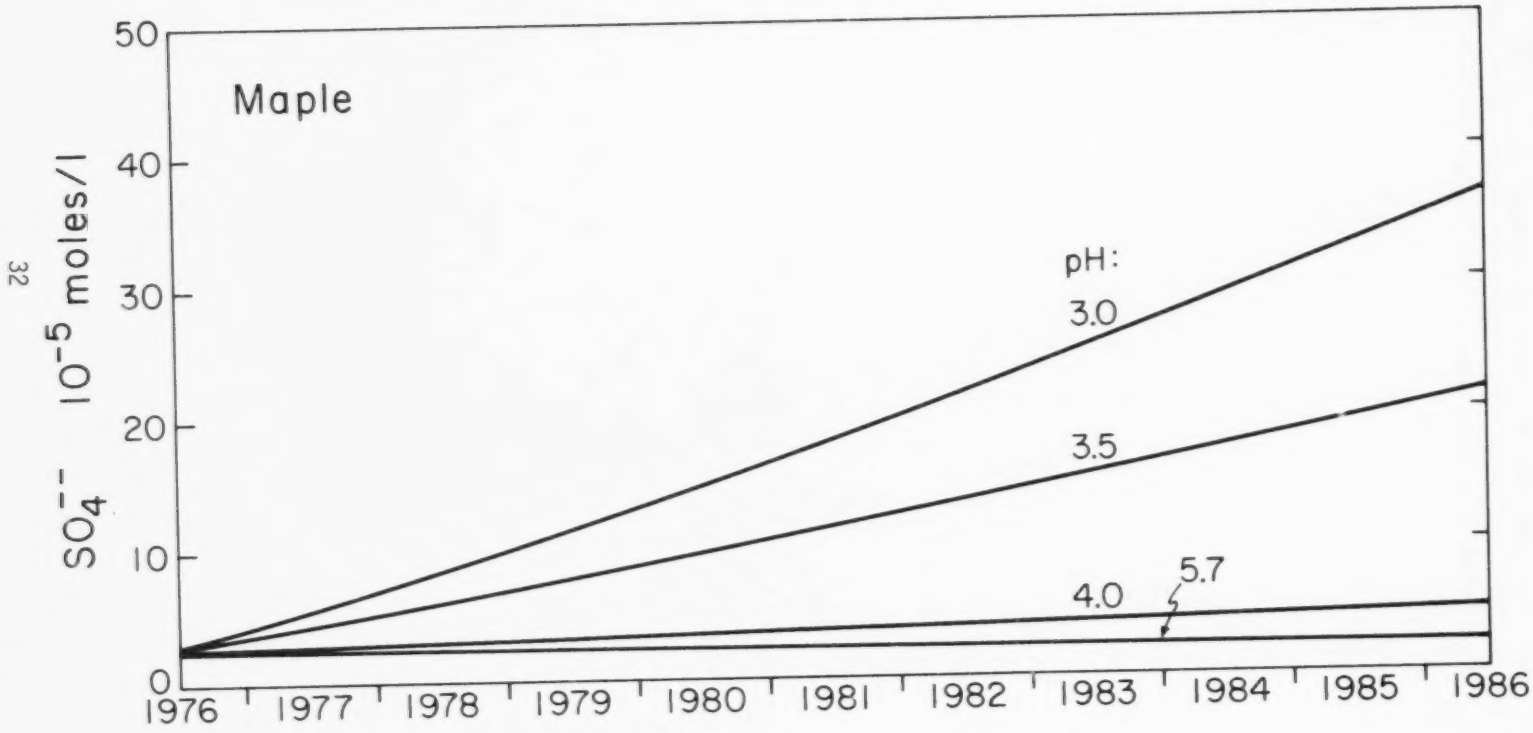



Figure 18. Simulated Time Series of 20-cm soil solution in maple plots. Results were produced by LEACH computer simulation model.

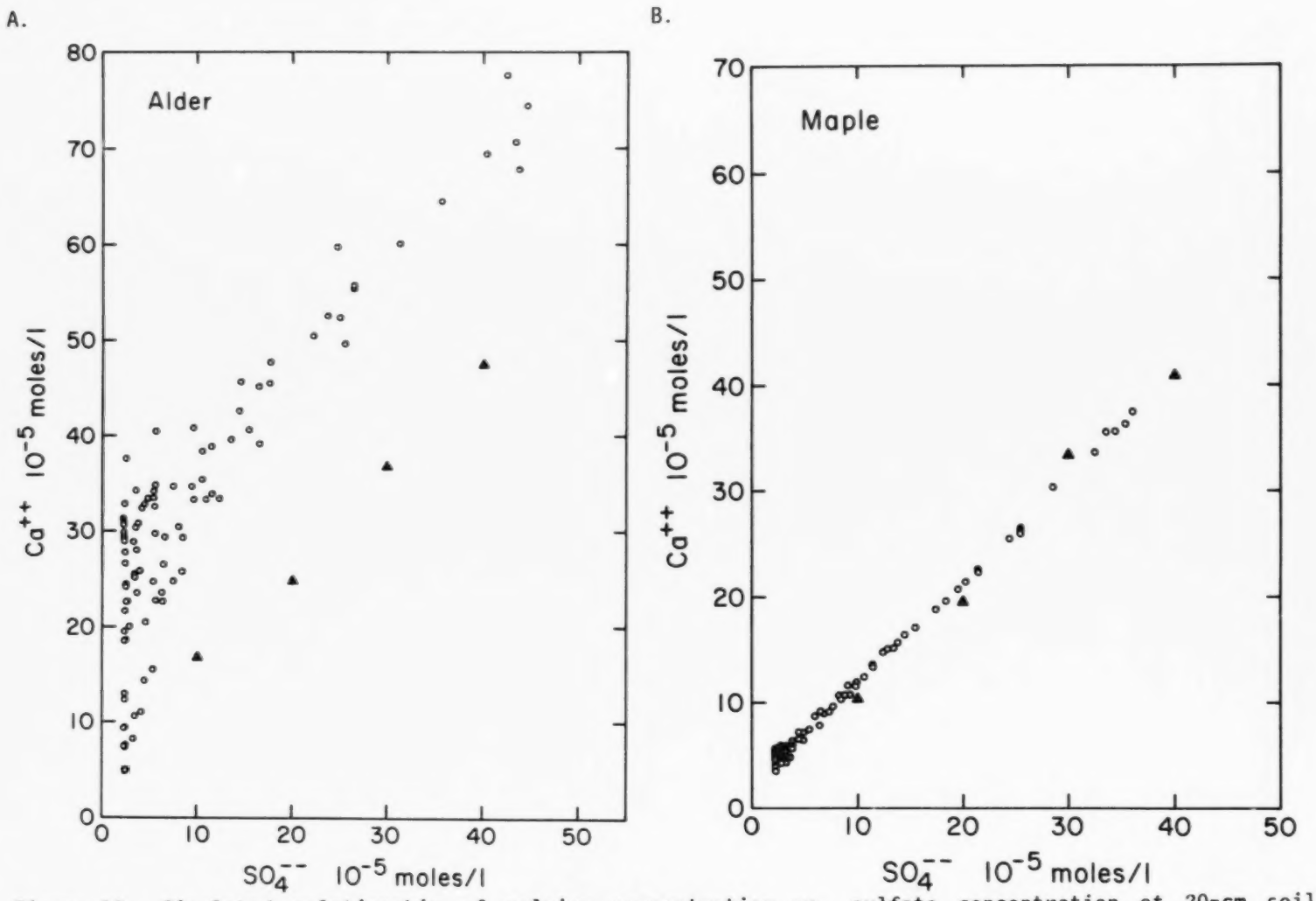



Figure 19. Simulated relationship of calcium concentration vs. sulfate concentration of 20-cm soil solution. Points represented by ( ● ) were produced by LEACH computer simulation model. Points represented by ( ▲ ) were extracted from data shown in Figures 13 and 14.

TABLE 4. RESULTS OF LEACH SIMULATION

| | Starting Value | Ending Value |
|---|---|---|
| pH | 5.3 | 4.9 |
| $H^+$ | 5 μeq/l | 12 μeq/l |
| $Ca^{2+}$ | 102 μeq/l | 750 μeq/l |
| $Al^{3+}$ | 0 μeq/l | 1 μeq/l |
| $SO_4^{2-}$ | 48 μeq/l | 726 μeq/l |
| $Cl^-$ | 55 μeq/l | 34 μeq/l |
| $HCO_3^-$ | 3 μeq/l | 1 μeq/l |
| Base Saturation | 12% | 12% |

All values except base saturation refer to the soil solution at 20 cm. Simulation used values in Table 3 for maple plots, and was for 10 years.

## REFERENCES


1. Bolin, B., L. Granat, L. Ingelstam, M. Johannesson, E. Mattsson, S. Oden, H. Rodhe and C. O. Tamm. 1971. Air pollution across national boundaries. The impact of sulfur in air and precipitation. Sweden's case study for the United Nations Conference on the Human Environment. P. A. Norstedt and Sons, Stockholm, Sweden. 97 pp.

2. Braekke, F. H. 1976. Impact of acid precipitation on forest and freshwater ecosystems in Norway. Research Report FR6/76. SNSF Project, As, Norway. 111 pp.

3. Cogbill, C. V. and G. E. Likens. 1974. Acid precipitation in northeastern United States. Water Resources Research 10:1133-1137.

4. Gambell, A. W. and D. W. Fisher. 1966. Chemical composition of rainfall, eastern North Carolina and southeastern Virginia. U.S. Geological Survey Water Supply Paper 1535-K. 41 pp.

5. Likens, G. E. and F. H. Bormann. 1974. Acid Rain: a serious regional environmental problem. Sci. 184:1176-1179.

6. Likens, G. E., R. E. Wright, J. N. Galloway and R. J. Butler. 1979. Acid rain. Sci. Am. 241:42-51.

7. Forest Service. 1976. Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem. USDA Forest Service General Technical Report NE-23, Northeastern Forest Experiment Station, Upper Darby, PA. 1974 pp.

8. Larson, T. V., R. J. Charlson, E. J. Knudson, G. D. Christian and H. Harrison. 1975. The influence of a sulfur dioxide point source on the rain chemistry of a single storm in the Puget Sound region. Water, Air and Soil Pollut. 4:319-328.

9. Liljestrand, H. M. and J. J. Morgan. 1978. Chemical composition of acid precipitation in Pasadena, Calif. Environ. Sci. Technol. 12:1271-1273.

10. McColl, J. G. and D. S. Bush. 1978. Precipitation and throughfall chemistry in the San Francisco Bay area. J. Environ. Qual. 7:352-357.

11. Forest Service. 1976. Workshop report on acid precipitation and the forest ecosystem. USDA Forest Service General Technical Report NE-26.

12. Galloway, J. N., E. B. Cowling, E. Gorham and W. W. McFee. 1978. A national program for assessing the problem of atmospheric deposition (acid rain). A report to the Council on Environmental Quality. Natural Resource Ecology Laboratory, Colorado State University, Ft. Collins.

13. Electric Power Research Institute (EPRI). 1979. Ecological effects of acid precipitation. Report of workshop held at Gatehouse-of-Fleet, Galloway, U.K., September 4-7, 1978. EPRI SOA77-403.

14. Wiklander, L. 1973. The acidification of soil by acid precipitation. Grundforbattring 26:155-164.

15. Wiklander, L. 1975. The role of neutral salts in the ion exchange between acid precipitation and soil. Geoderma 14:93-105.

16. Johnson, D. W. and D. W. Cole. 1977. Anion mobility in soils: relevance to nutrient transport from terrestrial to aquatic ecosystems. USEPA, Corvallis Environmental Research Laboratory, EPA-600/3-77-068, Corvallis, OR. 27 pp.

17. Reuss, J. 1978. Simulation of nutrient loss from soils due to rainfall acidity. U.S. EPA, Corvallis Environmental Research Laboratory, EPA-600/3-78-053, Corvallis, OR. 44 pp.

18. Crowther, C. and A. G. Ruston. 1911. The nature, distribution and effects upon vegetation of atmospheric impurities in and near an industrial town. J. of Agric. Sci. 4:25-55.

19. Overrein, L. N. 1972. Sulfur pollution patterns observed; leaching of calcium in forest soil determined. Ambio. 1:145-147.

20. Nyborg, M. and McMinnon, Allen and Associates, Ltd. 1973. Atmospheric sulfur dioxide: effects on the pH and sulfur content of rain and snow: addition of sulfur to surface waters, soil, and crops; and acidification of soils. In: D. Hocking and R. Reiter, eds., Proceedings of a workshop on sulfur gas research in Alberta. Information Report NOR-X-72. Northern Forest Research Centre, Edmonton, Canada.

21. Cronan, C. S. 1979. Effects of acid precipitation on soil leaching processes in high elevation forests of the northeastern U.S. In: H. H. Izard and J. S. Jacobson, eds., Scientific papers from the public meeting on acid precipitation, Lake Placid, NY. May 4-5, 1978. New York State Assembly, Albany.

22. Carroll, D. 1962. Rainwater as a chemical agent of geologic processes—a review. U.S. Geological Survey Water Supply Paper 1535-G. 18 pp.

23. Johnson, N. M., R. C. Reynolds and G. E. Likens. 1972. Atmospheric sulfur: its effect on the chemical weathering of New England. Sci. 177:514-516.

24. Norton, S. A. 1976. Changes in chemical processes in soils caused by acid precipitation. In: Proceedings of the first international symposium on acid precipitation and the forest ecosystem. USDA Forest Service General Technical Report NE-23.

25. Turk, J. T. and N. E. Peters. 1979. Acid rain weathering of a metasedimentary rock basin, Herkimer County, New York. In: H. H. Izard and J. S. Jacobson, eds., Scientific papers from the public meeting on acid precipitation, Lake Placid, NY. May 4-5, 1978. New York State Assembly, Albany.

26. Jonsson, B. and R. Sundberg. 1972. Has the acidification by atmospheric pollution caused a growth reduction in Swedish forests. Research Note No. 20. Department of Forest Yield Research, Royal College of Forestry, Stockholm, Sweden. 49 pp.

27. Jonsson, B. and R. Sundberg. 1976. Soil acidification by atmospheric pollution and forest growth. In: Proceedings of the First international symposium on acid precipitation and the forest ecosystem. USDA Forest Service General Technical Report NE-23.

28. Tamm, C. O. 1953. Growth, yield and nutrition in carpets of a forest moss (Hylocomium splendens). Medd. Stat. Skogsforskn. Inst. 43:1-140.

29. Madgwick, H. A. I. and J. D. Ovington. 1959. The chemical composition of precipitation in adjacent forest and open plots. Forestry 32:14-22.

30. Voigt, G. K. 1959. Distribution of rainfall under forest stands. Forest Sci. 6:2-10.

31. Voigt, G. K. 1960. Alteration of the composition of rainwater by trees. Amer. Midl. Nat. 63:321-326.

32. Carlisle, A., A. H. F. Brown and E. J. White. 1966. The organic matter and nutrient elements in precipitation beneath a Sessile Oak (Quercus petraea) canopy. J. Ecology 54:87-98.

33. Nihlgard, B. 1970. Precipitation, its chemical composition and effect on soil water in a beech and a spruce forest in south Sweden. Oikos 21:208-217.

34. Henderson, G. W., W. F. Harris, D. E. Todd and T. Grizzard. 1972. Quantity and chemistry of throughfall as influenced by forest-type and season. J. Ecology 65:365-374.

35. Eaton, J. S., G. E. Likens and F. H. Bormann. 1973. Throughfall and stemflow chemistry in a northern hardwood forest. J. Ecology 61:495-508.

36. Wood, T. and F. H. Bormann. 1975. Increases in foliar leaching caused by acidification of an artificial mist. Ambio. 4:169-171.

37. Wood, T. and F. H. Bormann. 1976. Short-term effects of an artificial acid rain upon the growth and nutrient relations of Pinus strobus L. In: Proceedings of the first international symposium on acid precipitation and the forest ecosystem. USDA Forest Service General Technical Report NE-23.

38. Mayer, R. and B. Ulrich. 1976. Acidity of precipitation as influenced by the filtering of atmospheric sulfur and nitrogen compounds—its role in the element balance and effect on soil. In: Proceedings of the first international symposium on acid precipitation and the forest ecosystem. USDA Forest Service General Technical Report NE-23.

39. Fairfax, J. A. W. and N. W. Lepp. 1976. The effect of simulated acid precipitation on cation losses from a range of tree litters. In: L. Karenlampi, ed., Proceedings of the Kuopio Meeting on plant damages caused by air pollution, August 16-18, 1976, University of Kuopio, Finland.

40. Lee, J. and D. E. Weber. 1976. A study of the effects of acid rain on model forest ecosystems. In: Proceedings of the annual meeting of the Air Pollution Control Assoc. Portland, OR., June 1976. 17 pp.

41. Hart, J. W. 1978. User manual for the LEACH acid rain simulation model. USEPA, Corvallis Environmental Research Laboratory, Corvallis, OR. CERL-046.

42. Likens, G. E. and F. H. Bormann. 1972. Nutrient cycling in ecosystems. In: Ecosystem Structure and Function, p. 25-47. Proc. 31st Annual Biology Colloquim, Oregon State University Press, Corvallis, OR.

43. Cronan, C. S., W. A. Reiners, R. C. Reynolds and G. E. Lang. 1978. Forest floor leaching: contributions from mineral, organic, and carbonic acids in New Hampshire subalpine forests. Sci. 200:304-311.

44. Koterba, M. T., J. W. Hornbeck and R. S. Pierce. 1979. Effects of sludge applications on soil water solutions and vegetation in a northern hardwood stand. J. Environ. Qual. 8:72-78.

45. Johnson, D. W. and D. W. Cole. 1976. Sulfate mobility in an outwash soil in western Washington. In: Proceedings of the first international symposium on acid precipitation and the forest ecosystem. USDA Forest Service General Technical Report NE-23.